

ZUMDAHL

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volume one

Chemistry

sixth edition



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STEVEN S.
ZUMDAHL

UNIVERSITY OF ILLINOIS

SUSAN A.
ZUMDAHL

UNIVERSITY OF ILLINOIS

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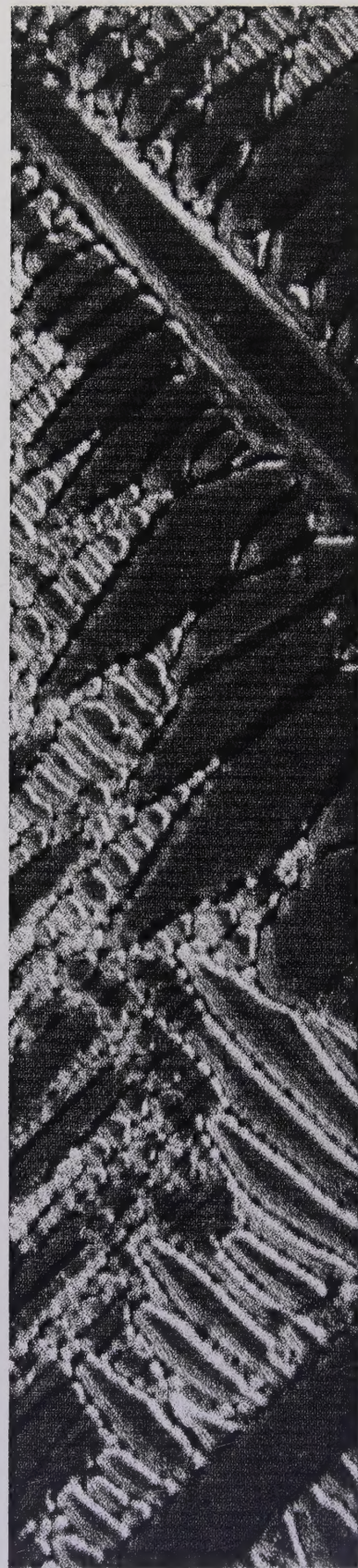
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To the Professor

Because of the positive response to the fifth edition of this text, the sixth edition of *Chemistry* continues in the same spirit: a presentation of the concepts of chemistry in a clear, interesting, and student-friendly manner. However, we have gone over every page in the fifth edition thoroughly, fine-tuning in some cases and substantially rewriting in others. In doing so, we have incorporated numerous constructive suggestions from instructors who used the previous edition.

Since visual material is especially important for learning general chemistry, which typically presents a pictorial view of chemical concepts, the art program has been revised extensively. Many new illustrations representing the microscopic world of chemistry have been added in this edition. Special illustrations and color photographs integrate descriptive chemistry with chemical principles, and many new **Chemical Impact** features emphasize practical applications of newly learned concepts.

Important Features of the Sixth Edition

- The new edition of *Chemistry* contains numerous discussions, illustrations, and exercises aimed at *overcoming common misconceptions*. It has become increasingly clear from our own teaching experience that students often struggle with chemistry because they misunderstand many of the fundamental concepts. In this text, we have gone to great lengths to provide illustrations and explanations aimed at giving students more accurate pictures of the fundamental ideas of chemistry. In particular, we have attempted to represent the microscopic world of chemistry so that students have a picture in their minds of “what the atoms and molecules are doing.” The expanded art program emphasizes this goal. Also, we have placed a larger emphasis on the qualitative understanding of concepts before quantitative problems are considered. Because using an algorithm to correctly solve a problem often masks misunderstanding—students assume they understand the material because they got the right “answer”—it is important to probe their understanding in other ways. In this vein we have included a number of conceptual questions at the end of each chapter that are intended for group discussion. It is our experience that students often learn the most when they teach each other. Students are forced to recognize their own lack of conceptual understanding when they try and fail to explain a concept to a colleague.
- With a strong *problem-solving orientation*, this text talks to the student about how to approach and solve chemical problems. We have made a strong pitch to students for using a thoughtful and logical approach rather than simply memorizing procedures. In particular, an innovative method is given for dealing with acid–base equilibria, the material the typical student finds most difficult and frustrating. The key to this approach involves first deciding what species are present in solution, then thinking about the chemical properties of these species. This method provides a general framework for approaching all types of solution equilibria.
- The text contains *almost 300 sample exercises*, with many more examples given in the discussions leading to sample exercises or used to illustrate general strategies. When a specific strategy is presented, it is summarized, and the sample exercise that follows it reinforces the step-by-step attack on the problem. In general, in approaching problem solving we emphasize understanding rather than an algorithm-based approach.
- We have presented a thorough *treatment of reactions* that occur in solution, including acid–base reactions. This material appears in Chapter 4, directly after the chapter on chemical stoichiometry, to emphasize the connection between solution reactions and chemical reactions in general. The early presentation of this material provides an opportunity to cover some interesting descriptive chemistry and also supports the lab, which typically involves a great deal of aqueous chemistry. Chapter 4 also includes oxidation–reduction reactions, because a large number of interesting and important chemical reactions involve redox processes. However, coverage of oxidation–reduction is optional at this point and depends on the needs of a specific course.
- *Descriptive chemistry* and chemical principles are thoroughly integrated in this text. Chemical models may appear sterile and confusing without the observations that stimulated their invention. On the other hand, facts without organizing principles may seem overwhelming. A combination of observations and models can make chemistry both interesting and understandable. In addition, in those chapters that deal with the chemistry of the elements systematically, we have made a continuous effort to show how properties and models correlate. Descriptive chemistry is presented in a variety of ways—as applications of the principles in separate sections, in sample exercises and exercise sets, in photographs, and in **Chemical Impact** features.
- Throughout the book a strong *emphasis on models* prevails. Coverage includes how they are constructed, how they are tested, and what we learn when they inevitably fail. Models are developed naturally, with pertinent observations always presented first to show why a particular model was invented.

- Everyday-life *applications* of chemistry that should be of interest to students taking general chemistry appear throughout the text. For example, the **Chemical Impact** “Fuel Cells for Cars” illustrates the chemistry behind cars powered by fuel cells, while “Nature Has Hot Plants” discusses several fascinating species of heat-producing plants, including the voodoo lily. Many industrial applications have also been incorporated into the text.
- A double-helix icon in the *Instructor’s Annotated Edition* highlights organic and biological examples of applications that are integrated throughout the text, in end-of-chapter problems, in exercises, or in-text discussions or examples. This feature allows instructors to quickly locate material that will be of particular interest to students in pre-medicine, biology, or other health-related fields.
- Judging from the favorable comments of instructors and students who have used the fifth edition, the text seemed to work very well in a variety of courses. We were especially pleased that *readability* was cited as a key strength when students were asked to assess the text. Thus, although the text has been fine-tuned in many areas, we have endeavored to build on the basic descriptions, strategies, analogies, and explanations that were successful in the previous editions.

New to the Sixth Edition

The sixth edition of *Chemistry* incorporates many significant improvements.

- The art program has been thoroughly revised to include many new molecular-level illustrations. New molecular-level art has been integrated into the text discussions and added to many end-of-chapter problems.
- The chapters near the end of the text have been reorganized. The chapter on nuclear chemistry has been moved from Chapter 21 to Chapter 18 in the sixth edition, and the biochemistry coverage in the fifth edition has been shortened and combined with the organic material to form a new Chapter 22 in the sixth edition. The descriptive chapters (19–21) have also been revised and updated to more accurately reflect the current teaching pedagogy.
- The end-of-chapter exercises and problems have been revised, providing approximately 20% new problems, including some that feature molecular art. End-of-chapter problems include: *In-Class Discussions Questions* to test students’ conceptual grasp of the material; *Questions* to help review important facts; *Exercises* that are paired and organized by topic; *Additional Exercises*, which are not

keyed by topic; *Challenge Problems*, which require students to combine skills and problems; and *Marathon Problems*, which are the most comprehensive and challenging type of problem.

- New *Media Activities* help integrate the extensive resources in the student technology package into the general chemistry course. These activities appear following the problems listed above.
- A large number of new **Chemical Impacts** have been included in the sixth edition to continue the emphasis on up-to-date application of chemistry in the real world. These essays feature intriguing topics such as “The Chemistry of Art” and “Farming the Wind” to highlight the applications of chemistry to everyday life.
- To support the use of active learning in chemical education, we have created new PowerPoint presentations that feature in-class discussion questions called *Reacts*, chemical demonstrations, animations, and figures from the text. This material is designed to help instructors present chemistry using an interactive teaching style, which we believe is most effective in promoting student learning. An *Interactive Course Guide* includes the discussion questions and supporting information in a workbook format. The questions are repeated in the workbook (with space to record answers) so that students can focus on participation in class sessions. This guide can then be used effectively for independent student review outside of class.
- The sixth edition of *Chemistry* also features a web site specific to the text. This site includes an archive of **Chemical Impacts** from previous editions of the text as well as the current Impacts. These Impacts have links to other sites providing more information on the topic under consideration. Other areas of the site feature biographical information on the people important to the development of chemistry, links from interesting general chemical sites to sites related to each chapter in the text, information on careers relevant to the chemical sciences, flashcards to help students study important terms, and an online library of molecules.
- A very important feature accompanying the sixth edition is a new system of Interactive Online Homework, powered by *EduSpace*®, that is structured to help students learn chemistry in a conceptual way. The system is modeled on a one-to-one teacher-student problem session. When a student cannot answer a given question, instead of giving him/her the correct answer, the student receives a hint. Often the hints are in the form of a question on which the student receives feedback. The philosophy behind the electronic homework is to help students understand the material so that they can arrive at the

correct answer by their own efforts, supported by the kind of help an instructor would provide in a one-to-one tutoring session.

Another important feature of this homework system is that each student, even in a very large course, receives a unique set of tasks for each homework assignment. This is accomplished using random number generators and several versions for tasks that contain specific chemical reactions and nonnumerical concepts. Each student's work is assessed by the system and the score for each task in the assignment is recorded in the electronic gradebook for immediate access by both student and instructor. The system also encourages increased student responsibility by setting firm deadlines for assignments. From the instructor's perspective, the system encourages student study without the burden of tracking student efforts through grading. Our experience with a similar system at the University of Illinois convinces us that this new homework system represents an important breakthrough in helping students learn chemistry.

Flexibility of Topic Order

The order of topics in the text was chosen because it is preferred by the majority of instructors. However, we consciously constructed the book so that many other orders are possible. At the University of Illinois, for a two-semester sequence we use the chapters in this order: 1–6, 13–15, 7–9, 18, 21, 12, 10, 11, 16, 17, and parts of 22. Sections of Chapters 19, 20, and parts of 22 are used throughout the two semesters as appropriate. This order, chosen because of the way the laboratory is organized, is not necessarily recommended, but it illustrates the flexibility of order built into the text.

Some specific points about topic order:

- About half of chemistry courses present kinetics before equilibria; the other half present equilibria first. This text is written to accommodate either order.
- The introductory aspects of thermodynamics are presented relatively early (in Chapter 6) because of the importance of energy in various chemical processes and models, but the more subtle thermodynamic concepts are left until later (Chapter 16). These two chapters may be used together if desired.
- To make the book more flexible, the derivation of the ideal gas law from the kinetic molecular theory and quantitative analysis using spectroscopy are presented in the appendixes. Although mainstream general chemistry courses typically do not cover this material, some courses may find it appropriate. By using the optional material in the appendixes and by assigning the more difficult end-of-chapter exercises (from the additional exercises section), an instructor will find the level of the text ap-

propriate for many majors courses or for other courses requiring a more extensive coverage of these topics.

- Because some courses cover bonding using only a Lewis structure approach, orbitals are not presented in the introductory chapter on bonding (Chapter 8). In Chapter 9 both hybridization and the molecular orbital model are covered, but either or both of these topics may be omitted if desired.
- Chapter 4 can be tailored to fit the specific course involved. Used in its entirety where it stands in the book, it provides interesting examples of descriptive chemistry and supports the laboratory program. Material in this chapter can also be skipped entirely or covered at some later point, whenever appropriate. For example, the sections on oxidation and reduction can be taught with electrochemistry. Although many instructors prefer early introduction of this concept, these sections can be omitted without complication since the next few chapters do not depend on this material.

Supplements

An extensive learning and teaching package has been designed to make this book more useful to both students and instructors.

For the Student

- *Technology Guide.* Automatically packaged with all new copies of Zumdahl, *Chemistry*, this handy guide provides information and access to the technology resources available with the sixth edition. Two passkeys, one for SMARTHINKING™ online tutoring and one for the Online Homework system, are included in the guide. Passkeys are valid for 12 months from initial sign-on. A user name and password are also included for access to the student web site.

General Chemistry Interactive Student CD-ROM. Highly interactive, offering topic summaries, conceptual enhancement, dynamic visualization, and more. Cross-platform (Macintosh/Windows) CD.

Media Activities. These end-of-chapter activities direct students to the technology resources provided to explore topics, learn concepts, and solve problems.

SMARTHINKING™ live, online tutoring (smarthinking.com/houghton.html). Passkey required and included. This partnership between Houghton Mifflin and SMARTHINKING.com provides students with live online personalized tutoring by qualified e-structors plus asynchronous access any time.

Student web site

(chemistry.college.hmco.com/students). User name and password required and included. Includes Houghton

Mifflin's ACE self-quizzing, interactive molecules, flashcards of key terms and concepts, problems linked to the text, *Chemical Impact* boxes, and links to other useful sites, including online homework.

Houghton Mifflin's EduSpace® Interactive Online Homework system. Passkey required. The Online Homework system provides students with problems, based on the textbook, with hints and feedback to simulate a one-on-one tutoring session. Individual student progress is tracked and may be viewed, managed, and downloaded by instructors.

- *eBook*, the complete text of *Chemistry*, Sixth Edition is available in electronic format for selected eBook readers. Contact your Houghton Mifflin representative for details.
- *Study Guide*, by Paul B. Kelter of the University of North Carolina—Greensboro. Written to be a self-study aid for students, this guide includes alternate strategies for solving problems, supplemental explanations for the most difficult material, and self-tests. There are approximately 500 worked examples and 1200 practice problems (with answers), designed to give students mastery and confidence.
- *Student Solutions Manual*, by Thomas J. Hummel, Susan Arena Zumdahl, and Steven S. Zumdahl, all of the University of Illinois, Urbana, provides detailed solutions for half of the end-of-chapter exercises (designated by the blue question numbers) using the strategies emphasized in the text. To ensure the accuracy of the solutions, this supplement and the *Complete Solutions Guide* were checked independently by several instructors.
- *Interactive Course Guide*, by Donald J. DeCoste. This printed workbook can be used in lecture or recitation in conjunction with the instructor PowerPoint slides. It provides a complete set of *React* questions with space for student answers. Students can use the workbook as a self-study aid outside of class.
- *Solving Equilibrium Problems with Applications to Qualitative Analysis*, by Steven S. Zumdahl. Successfully used by thousands of students over the last ten years, this book offers thorough, step-by-step procedures for solving problems related to equilibria taking place both in the gas phase and in solution. Containing hundreds of sample exercises, test exercises with complete solutions, and end-of-chapter exercises with answers, the text utilizes the same problem-solving methods found in *Chemistry* and is an excellent source of additional drill-type problems. The last chapter presents an exploratory qualitative analysis experiment with explanations based on the principles of aqueous equilibria.
- *Experimental Chemistry*, Sixth Edition, by James F. Hall of the University of Massachusetts—Lowell, provides an

extensively revised laboratory program compatible with the text. The 48 experiments present a wide variety of chemistry, and many experiments offer choices of procedures. Safety is strongly emphasized throughout the program.

For the Instructor

- *HM ClassPrep™ with HMTesing™ Version 6.0 CD-ROM* includes everything an instructor needs to develop lectures: PowerPoint slides with lecture outlines; all text figures, tables, and virtually all photos; as well as *Instructor's Resource Guide* (pdf format); *Test Bank* (MS Word files of the printed *Test Bank*); and animation and video files. It also includes a series of large-format animations and videos for use in the classroom.

HM Testing Version 6.0 combines a flexible test-editing program with a comprehensive gradebook function for easy administration and tracking. It enables instructors to administer tests via network server or the web. The *HM Testing* database can produce multiple-choice, true/false, fill-in-the-blank, and essay tests. Questions can be customized based on the chapter being covered, the question format, level of difficulty, and specific topics. *HM Testing* provides high security for accessing test questions and grades. Cross-platform for Macintosh and Windows.

- *Instructor web site at college.hmco.com* is a text-specific site designed for instructors that offers access to all student web site resources, downloadable PowerPoint slides for use in lectures, additional classroom resources, and relevant links.
- *Course Management Software* is available through *WebCT* and *Blackboard.com*. These two distributed learning systems allow instructors to create a virtual classroom without any knowledge of HTML. Features include: assessment tools, a gradebook, online file exchange between instructors and students, online syllabi, and course descriptions. The customized *Chemistry* cartridges feature quizzes, study materials, and exercises related to the text.
- *Complete Solutions Guide*, by Thomas J. Hummel, Susan Arena Zumdahl, and Steven S. Zumdahl, presents detailed solutions for all of the end-of-chapter exercises in the text for the convenience of faculty and staff involved in instruction and for instructors who wish their students to have solutions for all exercises. Departmental approval is required for the sale of the *Complete Solutions Guide* to students.
- *Instructor's Resource Guide*, by Donald J. DeCoste, includes suggestions for alternative orders of topics, solutions to the Marathon Problems, suggested responses to the In-Class Discussion Questions, amplification of strategies used in various chapters, suggested sources

of additional information, answers to *Reacts*, and a section on notes for teaching assistants.

- *Lecture Demonstration Guide*, by Fred Jurgens of the University of Wisconsin—Madison, lists the sources for over 750 classroom demonstrations that can be used in general chemistry courses. Icons in the margins of the *Instructor's Annotated Edition* of the text key the demonstrations to their corresponding text discussions.
- *Instructor's Resource Guide for Experimental Chemistry*, Sixth Edition, by James F. Hall, contains tips including hints on running experiments, approximate times for each experiment, and answers to all prelab and postlab questions posed in the laboratory guide.
- *Bibliobase* (www.bibliobase.com) allows instructors to create a completely customized lab manual by mixing and matching from 88 general chemistry labs—including all the labs from *Experimental Chemistry*—and 56 labs for the course in general, organic, and biochemistry. At the web site, instructors search through the database of labs, make their selections, organize the sequence of the manual, and submit their order via the Internet. Customized, printed, and bound lab manuals are delivered to the bookstore within weeks.
- *Test Item File*, by Steven S. Zumdahl, Susan Arena Zumdahl, and Donald J. DeCoste (available to adopters), offers a printed version of more than 2000 exam questions, 10 percent of which are new to this edition, referenced to the appropriate text section. Questions are in multiple-choice, open-ended, and true-false formats.
- *Transparencies*, in a full-color set of 255, are available to adopters of the sixth edition of the text.
- *Houghton Mifflin Chemistry Videodiscs Volumes I and II* contain video clips of lecture demonstrations, animations of important chemical processes and concepts, and still images from the text that can be used in classroom presentations. Both discs are available free to adopters of the sixth edition.
- *Houghton Mifflin Videotapes Series A, B, C, and D* provide over 100 lecture demonstrations performed by John Luoma, Cleveland State University; John J. Fortman and Rubin Battino, Wright State University; Patricia L. Samuel, Boston University; and Paul Kelter, University of North Carolina—Greensboro.
- *General Chemistry DVD*. This disc contains the animations on the *Chemistry Video and Animations* CD-ROM and on the *Lecture Hall Animations* CD-ROM, plus the videos on videotape Series C.

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To the Student

The major purpose of this book, of course, is to help you learn chemistry. However, this main thrust is closely linked to two other goals: to show how important and how interesting the subject is, and to show how to think like a chemist. To solve complicated problems the chemist uses logic, trial and error, intuition, and, above all, patience. A chemist is used to being wrong. The important thing is to learn from a mistake, recheck assumptions, and try again. A chemist thrives on puzzles that seem to defy solutions.

Many of you using this text do not plan to be practicing chemists. However, the nonchemist can benefit from the chemist's attitude. Problem solving is important in all professions and in all walks of life. The techniques you will learn from this book will serve you well in any career you choose. Thus, we believe that the study of chemistry has much to offer the nonmajor, including an understanding of many fascinating and important phenomena and a chance to hone problem-solving skills.

This book attempts to present chemistry in a manner that is sensible to the novice. Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book the concepts are developed in a natural way: The observations come first and then models are constructed to explain the observed behavior.

Models are a major focus in this book. The uses and limitations of models are emphasized, and science is treated as a human activity, subject to all the normal human foibles. Mistakes are discussed as well as successes.

A central theme of this book is a thoughtful, systematic approach to problem solving. Learning encompasses much more than simply memorizing facts. Truly educated people use their factual knowledge as a starting point—a base for creative approaches to solving problems.

Read through the material in the text carefully. For most concepts, illustrations or photos will help you visualize what is going on. To further help you visualize concepts by using animations and videos, we have packaged a CD-ROM, *General Chemistry: Interactive*, with your text. CD icons in the text margin signal that there is companion material available on the CD.

Often a given type of problem is “walked through” in the text before the corresponding sample exercises appear. Strategies for solving problems are given throughout the text.

Thoroughly examine the sample exercises and the problem-solving strategies. The strategies summarize the approach taken in the text; the sample exercises follow the strategies step-by-step. Schematics in Chapter 15 also illustrate the logical pathways to solving aqueous equilibrium problems.

Throughout the text, we have used margin notes to highlight key points, to comment on an application of the text material, or to reference material in other parts of the book. **Chemical Impact**, the boxed feature that appears frequently throughout the text, discusses especially interesting applications of chemistry to the everyday world.

Each chapter has a summary and key terms list for review, and the glossary gives a quick reference for definitions.

Learning chemistry requires working the end-of-chapter exercises assigned by your professor. Answers to exercises denoted by blue question numbers are in the back of the book, and complete solutions to those exercises are in the *Partial Solutions Guide*. To help you assess your level of proficiency, the *student web site* (www.college.hmco.com) offers quizzes and electronic homework assignments that feature instant feedback.

The *Study Guide* contains extra practice problems and many worked examples. The supplement, *Solving Equilibrium Problems with Applications to Qualitative Analysis*, reinforces in great detail the text's step-by-step approach to solving equilibrium problems and contains many worked examples and self-quiz questions.

It is very important to use the exercises and electronic homework assignments to your best advantage. Your main goal should not be to simply get the correct answer but to *understand the process* for getting the answer. Memorizing the solutions for specific problems is not a very good way to prepare for an exam. There are too many pigeonholes required to cover every possible problem type. Look within the problem for the solution. Use the concepts you have learned along with a systematic, logical approach to find the solution. Learn to trust yourself to think it out. You will make mistakes, but the important thing is to learn from these errors. The only way to gain confidence is to do lots of practice problems and use these to diagnose your weaknesses.

Be patient and thoughtful and work hard to understand rather than simply memorize. We wish you an interesting and satisfying year.



Chemical Foundations

1

When you start your car, do you think about chemistry? Probably not, but you should. The power to start your car is furnished by a lead storage battery. How does this battery work, and what does it contain? When a battery goes dead, what does that mean? If you use a friend's car to "jump start" your car, did you know that your battery could explode? How can you avoid such an unpleasant possibility? What is in the gasoline that you put in your tank, and how does it furnish the energy to drive to school? What is the vapor that comes out of the exhaust pipe, and why does it cause air pollution? Your car's air conditioner might have a substance in it that is leading to the destruction of the ozone layer in the upper atmosphere. What are we doing about that? And why is the ozone layer important anyway?

All these questions can be answered by understanding some chemistry. In fact, we'll consider the answers to all these questions in this text.

Chemistry is around you all the time. You are able to read and understand this sentence because chemical reactions are occurring in your brain. The food you ate for breakfast or lunch is now furnishing energy through chemical reactions. Trees and grass grow because of chemical changes.

Chemistry also crops up in some unexpected places. When archaeologist Luis Alvarez was studying in college, he probably didn't realize that the chemical elements iridium and niobium would make him very famous when they helped him solve the problem of the disappearing dinosaurs. For decades scientists had wrestled with the mystery of why the dinosaurs, after ruling the earth for millions of years, suddenly became extinct 65 million years ago. In studying core samples of rocks dating back to that period, Alvarez and his coworkers recognized unusual levels of iridium and niobium in these samples—levels much more characteristic of extraterrestrial bodies than of the earth. Based on these observations, Alvarez hypothesized that a large meteor hit the earth 65 million years ago, changing atmospheric conditions so

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1.1 Chemistry: An Overview

- *Science: A Process for Understanding Nature and Its Changes*

1.2 The Scientific Method

1.3 Units of Measurement

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- *Precision and Accuracy*

1.5 Significant Figures and Calculations

1.6 Dimensional Analysis

1.7 Temperature

1.8 Density

1.9 Classification of Matter

Male Monarch butterflies use the pheromones produced by a gland on their wings to make themselves attractive to females.

much that the dinosaurs' food couldn't grow, and they died—almost instantly in the geologic timeframe.

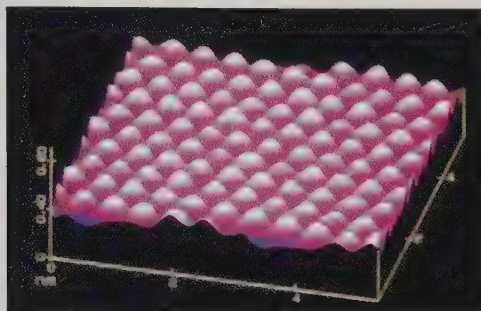
Chemistry is also important to historians. Did you realize that lead poisoning probably was a significant contributing factor to the decline of the Roman Empire? The Romans had high exposure to lead from lead-glazed pottery, lead water pipes, and a sweetening syrup called *sapa* that was prepared by boiling down grape juice in lead-lined vessels. It turns out that one reason for *sapa*'s sweetness was lead acetate (“sugar of lead”) that formed as the juice was cooked down. Lead poisoning with its symptoms of lethargy and mental malfunctions certainly could have contributed to the demise of the Roman society.

Chemistry is also apparently very important in determining a person's behavior. Various studies have shown that many personality disorders can be linked directly to imbalances of trace elements in the body. For example, studies on the inmates at Stateville Prison in Illinois link low cobalt levels with violent behavior. Lithium salts have been shown to be very effective in controlling the effects of manic depressive disease, and you've probably at some time in your life felt a special “chemistry” for another person. Studies suggest there is literally chemistry going on between two people who are attracted to each other. “Falling in love” apparently causes changes in the chemistry of the brain; chemicals are produced that give that “high” associated with a new relationship. Unfortunately, these chemical effects seem to wear off over time, even if the relationship persists and grows.

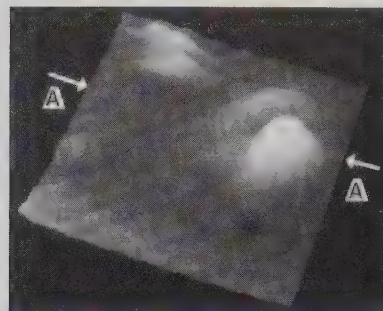
The importance of chemistry in the interactions of people should not really surprise us, since we know that insects communicate by emitting and receiving chemical signals via molecules called *pheromones*. For example, ants have a very complicated set of chemical signals to signify food sources, danger, and so forth. Also, various female sex attractants have been isolated and used to lure males into traps to control insect populations. It would not be surprising if humans also emitted chemical signals that we were not aware of on a conscious level. Thus chemistry is pretty interesting and pretty important. The main goal of this text is to help you understand the concepts of chemistry so that you can better appreciate the world around you and can be more effective in whatever career you choose.

1.1 Chemistry: An Overview

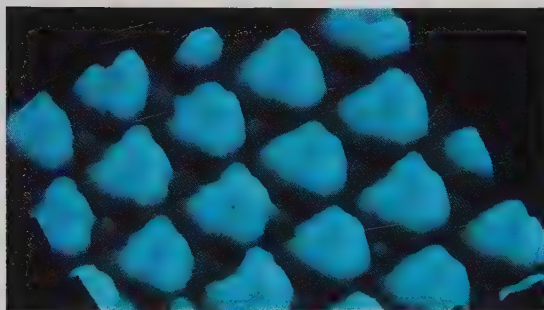
Since the time of the ancient Greeks, people have wondered about the answer to the question: What is matter made of? For a long time humans have believed that matter is composed of atoms, and in the previous three centuries we have collected much indirect evidence to support this belief. Very recently, something exciting has happened—for the first time we can “see” individual atoms. Of course, we cannot see atoms with the naked eye but must use a special microscope called a scanning tunneling microscope (STM). Although we will not consider the details of its operation here, the STM uses an electron current from a tiny needle to probe the surface of a substance. The STM pictures of several substances are shown in Fig. 1.1. Notice how the atoms are connected to one another by “bridges,” which, as we will see, represent the electrons that interconnect atoms.



(a)



(b)



(c)

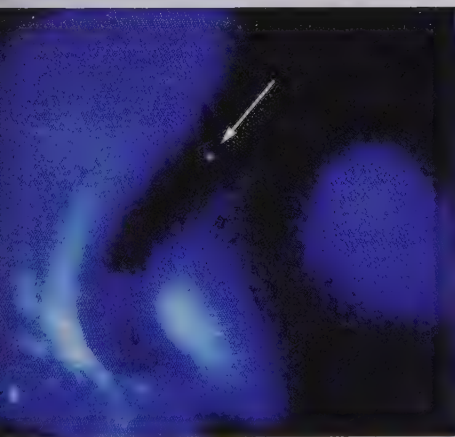
FIGURE 1.1

(a) The surface of a single grain of table salt. (b) An oxygen atom (indicated by arrow) on a gallium arsenide surface. (c) Scanning tunneling microscope image showing rows of ring-shaped clusters of benzene molecules on a rhodium surface. Each “doughnut”-shaped image represents a benzene molecule.

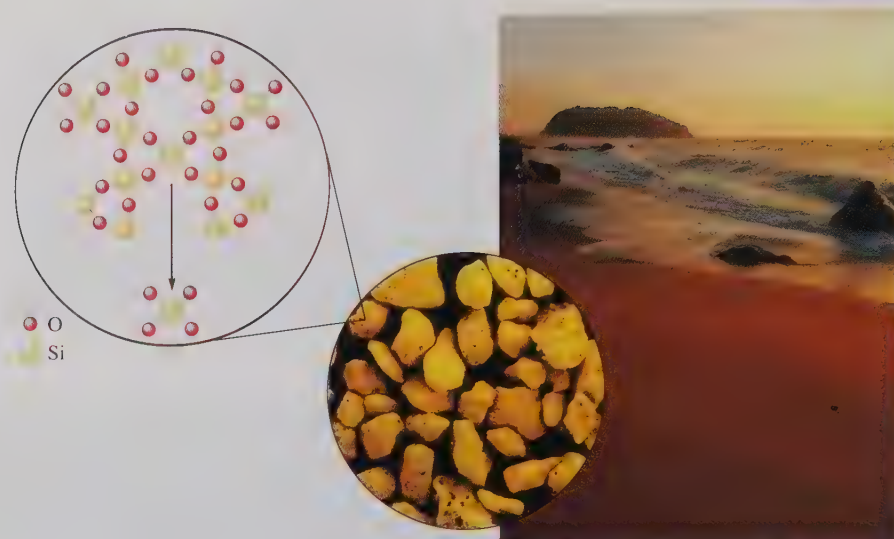
In addition to “seeing” the atoms in solids such as salt and gallium arsenide, we have learned how to isolate and view a single atom. For example, the tiny white dot in the center of Fig. 1.2 is a single mercury atom that is held in a special trap.

So, at this point, we are fairly sure that matter consists of individual atoms. The nature of these atoms is quite complex, and the components of atoms don’t behave much like the objects we see in the world of our experience. We call this world the *macroscopic world*—the world of cars, tables, baseballs, rocks, oceans, and so forth. One of the main jobs of a scientist is to delve into the macroscopic world and discover its “parts.” For example, when you view a beach from a distance, it looks like a continuous solid substance. As you get closer, you see that the beach is really made up of individual grains of sand. As we examine these grains of sand, we find they are composed of silicon and oxygen atoms connected to each other to form intricate shapes (see Fig. 1.3). One of the main challenges of chemistry is to understand the connection between the macroscopic world that we experience and the *microscopic world* of atoms and molecules. To truly understand chemistry you must learn to think on the atomic level. We will spend much time in this text helping you learn to do that.

One of the amazing things about our universe is that the tremendous variety of substances we find there results from only about 100 different kinds of atoms. You can think of these approximately 100 atoms as the letters in an alphabet out of which all the “words” in the universe are made. It is the way the atoms are organized in a

**FIGURE 1.2**

A charged mercury atom shows up as a tiny white dot (indicated by the arrow).

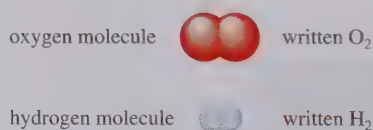
**FIGURE 1.3**

Sand on a beach looks uniform from a distance, but up close the irregular sand grains are visible, and each grain is composed of tiny atoms.

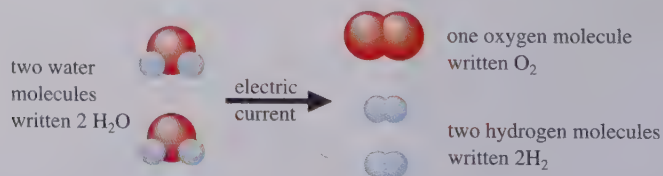
given substance that determines the properties of that substance. For example, water, one of the most common and important substances on earth, is composed of two types of atoms: hydrogen and oxygen. There are two hydrogen atoms and one oxygen atom bound together to form the water molecule:



When an electric current passes through it, water is decomposed to hydrogen and oxygen. These *chemical elements* themselves exist naturally as diatomic (two-atom) molecules:



We can represent the decomposition of water to its component elements, hydrogen and oxygen, as follows:



Notice that it takes two molecules of water to furnish the right number of oxygen and hydrogen atoms to allow for the formation of the two-atom molecules. This reaction explains why the battery in your car can explode if you jump start it improperly. When you hook up the jumper cables, current flows through the dead battery, which contains water (and other things), and causes hydrogen and oxygen to

CHEMICAL IMPACT

The Chemistry of Art

The importance of chemistry can show up in some unusual places. For example, a knowledge of chemistry is crucial to authenticating, preserving, and restoring art objects. The J. Paul Getty Museum in Los Angeles has a state-of-the-art chemical laboratory that cost many millions of dollars and employs many scientists. The National Gallery of Art (NGA) in Washington, D.C., also operates a highly sophisticated laboratory that employs 10 people: five chemists, a botanist, an art historian, a technician with a chemistry degree, and two fellows (interns).

One of the chemists at NGA is Barbara Berrie, who specializes in identifying paint pigments. One of her duties is to analyze a painting to see whether the paint pigments are appropriate for the time the picture was supposedly painted and consistent with the pigments known to be used by the artist given credit for the painting. This analysis is one way

in which paintings can be authenticated. One of Berrie's recent projects was to analyze the 1617 oil painting *St. Cecilia and an Angel*. Her results showed the painting was the work of two artists of the time, Orazio Gentileschi and Giovanni Lanfranco. Originally the work was thought to be by Gentileschi alone.

Berrie is also working to define the range of colors used by water colorist Winslow Homer (the NGA has 30 Homer paintings in its collection) and to show how his color palette changed over his career. In addition, she is exploring how acidity affects the decomposition of a particular deep green transparent pigment (called copper resinate) used by Italian Renaissance artists so that paintings using this pigment can be better preserved.

Berrie says, "The chemistry I do is not hot-dog chemistry, just good old-fashioned general chemistry."



Igniting soap bubbles filled with a mixture of hydrogen and oxygen.

form by decomposition of some of the water. A spark can cause this accumulated hydrogen and oxygen to explode, forming water again.



This example illustrates two of the fundamental concepts of chemistry: (1) matter is composed of various types of atoms, and (2) one substance changes to another by reorganizing the way the atoms are attached to each other.

These are core ideas of chemistry, and we will have much more to say about them.

Science: A Process for Understanding Nature and Its Changes

How do you tackle the problems that confront you in real life? Think about your trip to school. If you live in a city, traffic is undoubtedly a problem you confront daily. How do you decide the best way to drive to school? If you are new in town, you first get a map and look at the possible ways to make the trip. Then you might collect information from people who know the area about the advantages and disadvantages of various routes. Based on this information, you probably try to predict the best route. However, you can find the best route only by trying several of them and comparing the results. After a few experiments with the various possibilities, you probably will be able to select the best way. What you are doing in solving this everyday problem is applying the same process that scientists use to study

nature. The first thing you did was collect relevant data. Then you made a prediction, and then you tested it by trying it out. This process contains the fundamental elements of science.

1. Making observations (collecting data)
2. Making a prediction (formulating a hypothesis)
3. Doing experiments to test the prediction (testing the hypothesis)

Scientists call this process the *scientific method*. We will discuss it in more detail in the next section. One of life's most important activities is solving problems—not “plug and chug” exercises, but real problems—problems that have new facets to them, that involve things you may have never confronted before. The more creative you are at solving these problems, the more effective you will be in your career and your personal life. Part of the reason for learning chemistry, therefore, is to become a better problem solver. Chemists are usually excellent problem solvers, because to master chemistry, you have to master the scientific approach. Chemical problems are frequently very complicated—there is usually no neat and tidy solution. Often it is difficult to know where to begin.

1.2 The Scientific Method

Science is a framework for gaining and organizing knowledge. Science is not simply a set of facts but also a plan of action—a *procedure* for processing and understanding certain types of information. Scientific thinking is useful in all aspects of life, but in this text we will use it to understand how the chemical world operates. As we have said in our previous discussion, the process that lies at the center of scientific inquiry is called the **scientific method**. There are actually many scientific methods, depending on the nature of the specific problem under study and on the particular investigator involved. However, it is useful to consider the following general framework for a generic scientific method (see Fig. 1.4):

Steps in the Scientific Method

- ➡ **1 Making observations.** Observations may be *qualitative* (the sky is blue; water is a liquid) or *quantitative* (water boils at 100°C; a certain chemistry book weighs 2 kilograms). A qualitative observation does not involve a number. A quantitative observation (called a **measurement**) involves both a number and a unit.
- ➡ **2 Formulating hypotheses.** A **hypothesis** is a *possible* explanation for an observation.
- ➡ **3 Performing experiments.** An experiment is carried out to test a hypothesis. This involves gathering new information that enables a scientist to decide whether the hypothesis is valid—that is, whether it is supported by the new information learned from the experiment. Experiments always produce new observations, and this brings the process back to the beginning again.

To understand a given phenomenon, these steps are repeated many times, gradually accumulating the knowledge necessary to provide a possible explanation of the phenomenon.

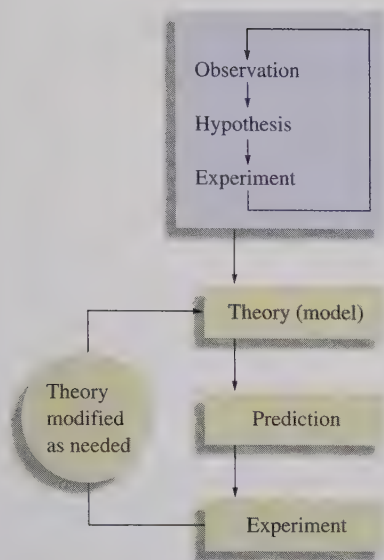


FIGURE 1.4
The fundamental steps of the scientific method.

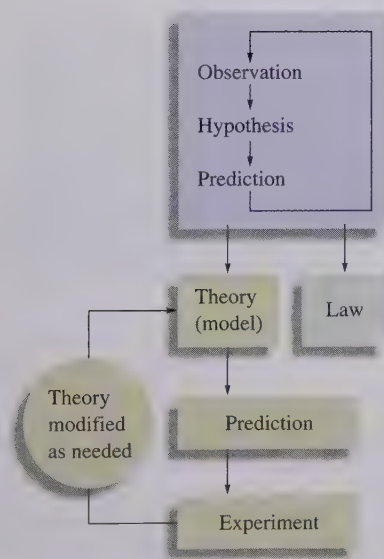


FIGURE 1.5
The various parts of the scientific method.

Once a set of hypotheses that agrees with the various observations is obtained, the hypotheses are assembled into a theory. A **theory**, which is often called a **model**, is a set of tested hypotheses that gives an overall explanation of some natural phenomenon.

It is very important to distinguish between observations and theories. An observation is something that is witnessed and can be recorded. A theory is an *interpretation*—a possible explanation of *why* nature behaves in a particular way. Theories inevitably change as more information becomes available. For example, the motions of the sun and stars have remained virtually the same over the thousands of years during which humans have been observing them, but our explanations—our theories—for these motions have changed greatly since ancient times. (See the Chemical Impact on Observations, Theories, and the Planets on the Web site.)

The point is that scientists do not stop asking questions just because a given theory seems to account satisfactorily for some aspect of natural behavior. They continue doing experiments to refine or replace the existing theories. This is generally done by using the currently accepted theory to make a prediction and then performing an experiment (making a new observation) to see whether the results bear out this prediction.

Always remember that theories (models) are human inventions. They represent attempts to explain observed natural behavior in terms of human experiences. A theory is actually an educated guess. We must continue to do experiments and to refine our theories (making them consistent with new knowledge) if we hope to approach a more nearly complete understanding of nature.

As scientists observe nature, they often see that the same observation applies to many different systems. For example, studies of innumerable chemical changes have shown that the total observed mass of the materials involved is the same before and after the change. Such generally observed behavior is formulated into a statement called a **natural law**. For example, the observation that the total mass of materials is not affected by a chemical change in those materials is called the **law of conservation of mass**.

Note the difference between a natural law and a theory. A natural law is a summary of observed (measurable) behavior, whereas a theory is an explanation of behavior. A *law summarizes what happens*; a *theory (model) is an attempt to explain why it happens*.

In this section we have described the scientific method as it might ideally be applied (see Fig. 1.5). However, it is important to remember that science does not always progress smoothly and efficiently. For one thing, hypotheses and observations are not totally independent of each other, as we have assumed in the description of the idealized scientific method. The coupling of observations and hypotheses occurs because once we begin to proceed down a given theoretical path, our hypotheses are unavoidably couched in the language of that theory. In other words, we tend to see what we expect to see and often fail to notice things that we do not expect. Thus the theory we are testing helps us because it focuses our questions. However, at the very same time, this focusing process may limit our ability to see other possible explanations.

It is also important to keep in mind that scientists are human. They have prejudices; they misinterpret data; they become emotionally attached to their theories and thus lose objectivity; and they play politics. Science is affected by profit motives, budgets, fads, wars, and religious beliefs. Galileo, for example, was forced to recant his astronomical observations in the face of strong religious resistance.



Robert Boyle (1627–1691) was born in Ireland. He became especially interested in experiments involving air and developed an air pump with which he produced evacuated cylinders. He used these cylinders to show that a feather and a lump of lead fall at the same rate in the absence of air resistance and that sound cannot be produced in a vacuum. His most famous experiments involved careful measurements of the volume of a gas as a function of pressure. In his book *The Skeptical Chymist*, Boyle urged that the ancient view of elements as mystical substances should be abandoned and that an element should instead be defined as anything that cannot be broken down into simpler substances. This conception was an important step in the development of modern chemistry.

Lavoisier, the father of modern chemistry, was beheaded because of his political affiliations. Great progress in the chemistry of nitrogen fertilizers resulted from the desire to produce explosives to fight wars. The progress of science is often affected more by the frailties of humans and their institutions than by the limitations of scientific measuring devices. The scientific methods are only as effective as the humans using them. They do not automatically lead to progress.

1.3 Units of Measurement

Making observations is fundamental to all science. A quantitative observation, or *measurement*, always consists of two parts: a *number* and a scale (called a *unit*). Both parts must be present for the measurement to be meaningful.

In this textbook we will use measurements of mass, length, time, temperature, electric current, and the amount of a substance, among others. Scientists recognized long ago that standard systems of units had to be adopted if measurements were to be useful. If every scientist had a different set of units, complete chaos would result. Unfortunately, different standards were adopted in different parts of the world. The two major systems are the *English system* used in the United States and the *metric system* used by most of the rest of the industrialized world. This duality causes a good deal of trouble; for example, parts as simple as bolts are not interchangeable between machines built using the two systems. As a result, the United States has begun to adopt the metric system.



Soda is commonly sold in 2-liter bottles—an example of the use of SI units in everyday life.

TABLE 1.1 The Fundamental SI Units

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Luminous intensity	candela	cd

TABLE 1.2 The Prefixes Used in the SI System (Those most commonly encountered are shown in blue.)

Prefix	Symbol	Meaning	Exponential Notation*
exa	E	1,000,000,000,000,000,000	10^{18}
peta	P	1,000,000,000,000,000	10^{15}
tera	T	1,000,000,000,000	10^{12}
giga	G	1,000,000,000	10^9
mega	M	1,000,000	10^6
kilo	k	1,000	10^3
hecto	h	100	10^2
deka	da	10	10^1
—	—	1	10^0
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000001	10^{-6}
nano	n	0.000000001	10^{-9}
pico	p	0.000000000001	10^{-12}
femto	f	0.000000000000001	10^{-15}
atto	a	0.000000000000000001	10^{-18}

*See Appendix 1.1 if you need a review of exponential notation.

TABLE 1.3 Some Examples of Commonly Used Units

Length	A dime is 1 mm thick. A quarter is 2.5 cm in diameter. The average height of an adult man is 1.8 m.
Mass	A nickel has a mass of about 5 g. A 120-lb person has a mass of about 55 kg.
Volume	A 12-oz can of soda has a volume of about 360 mL.

Most scientists in all countries have for many years used the metric system. In 1960, an international agreement set up a system of units called the *International System* (*le Système International* in French), or the **SI system**. This system is based on the metric system and units derived from the metric system. The fundamental SI units are listed in Table 1.1. We will discuss how to manipulate these units later in this chapter.

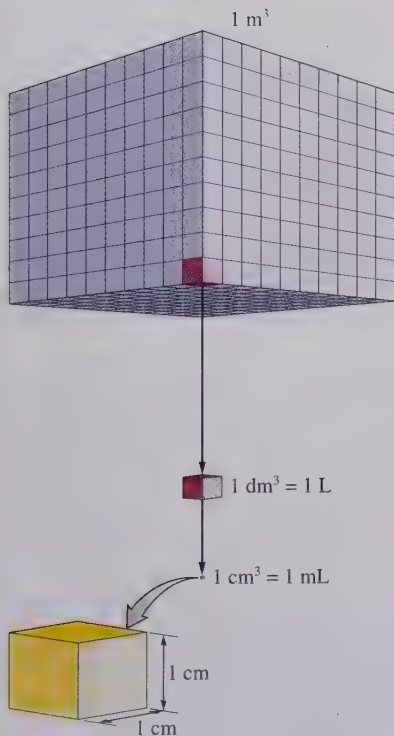
Because the fundamental units are not always convenient (expressing the mass of a pin in kilograms is awkward), prefixes are used to change the size of the unit. These are listed in Table 1.2. Some common objects and their measurements in SI units are listed in Table 1.3.

One physical quantity that is very important in chemistry is *volume*, which is not a fundamental SI unit but is derived from length. A cube that measures 1 meter (m) on each edge is represented in Fig. 1.6. This cube has a volume of $(1 \text{ m})^3 = 1 \text{ m}^3$. Recognizing that there are 10 decimeters (dm) in a meter, the volume of this cube is $(1 \text{ m})^3 = (10 \text{ dm})^3 = 1000 \text{ dm}^3$. A cubic decimeter, that is $(1 \text{ dm})^3$, is commonly called a *liter* (L), which is a unit of volume slightly larger than a quart. As shown in Fig. 1.6, 1000 liters are contained in a cube with a volume of 1 cubic meter. Similarly, since 1 decimeter equals 10 centimeters (cm), the liter can be divided into 1000 cubes each with a volume of 1 cubic centimeter:

$$1 \text{ liter} = (1 \text{ dm})^3 = (10 \text{ cm})^3 = 1000 \text{ cm}^3$$

FIGURE 1.6

The largest cube has sides 1 m in length and a volume of 1 m^3 . The middle-sized cube has sides 1 dm in length and a volume of 1 dm^3 , or 1 L. The smallest cube has sides 1 cm in length and a volume of 1 cm^3 , or 1 mL.



CHEMICAL IMPACT

Critical Units!

How important are conversions from one unit to another? If you ask the National Aeronautics and Space Administration (NASA), very important! In 1999 NASA lost a \$125 million Mars Climate Orbiter because of a failure to convert from English to metric units.

The problem arose because two teams working on the Mars mission were using different sets of units. NASA's scientists at the Jet Propulsion Laboratory in Pasadena, California, assumed that the thrust data for the rockets on the Orbiter they received from Lockheed Martin Astronautics in Denver, which built the spacecraft, were in metric units. In reality, the units were English. As a result the Orbiter dipped 100 kilometers lower into the Mars atmosphere than planned and the friction from the atmosphere caused the craft to burn up.

NASA's mistake refueled the controversy over whether Congress should require the United States to switch to the metric system. About 95% of the world now uses the metric system, and the United States is slowly switching from English to metric. For example, the automobile industry has adopted metric fasteners and we buy our soda in two-liter bottles.

Units can be very important. In fact, they can mean the difference between life and death on some occasions. In 1983, for example, a Canadian jetliner almost ran out of fuel when someone pumped 22,300 pounds of fuel into the aircraft instead of 22,300 kilograms. Remember to watch your units!



Artist's conception of the lost Mars Climate Orbiter.

Also, since $1 \text{ cm}^3 = 1 \text{ milliliter (mL)}$,

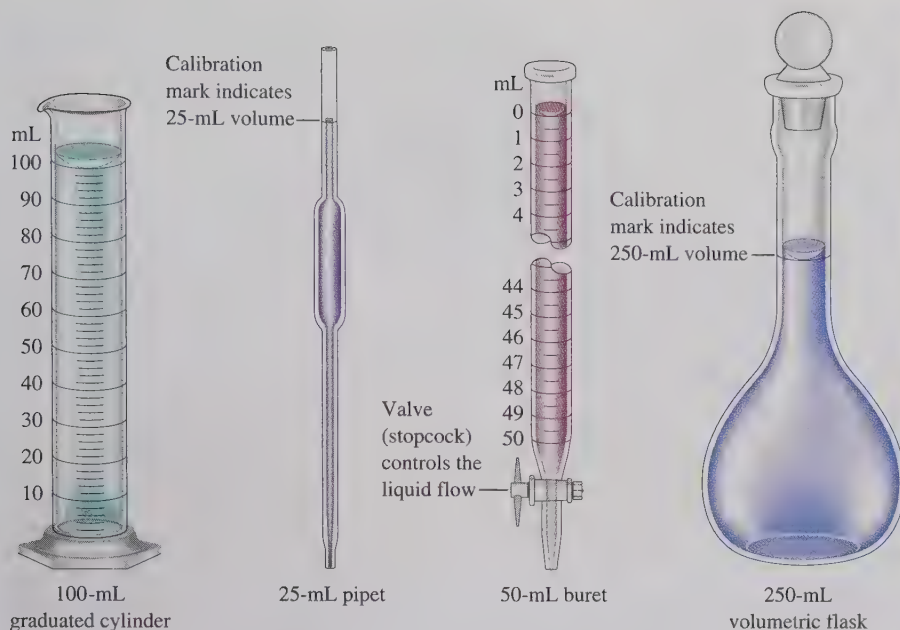
$$1 \text{ liter} = 1000 \text{ cm}^3 = 1000 \text{ mL}$$

Thus 1 liter contains 1000 cubic centimeters, or 1000 milliliters.

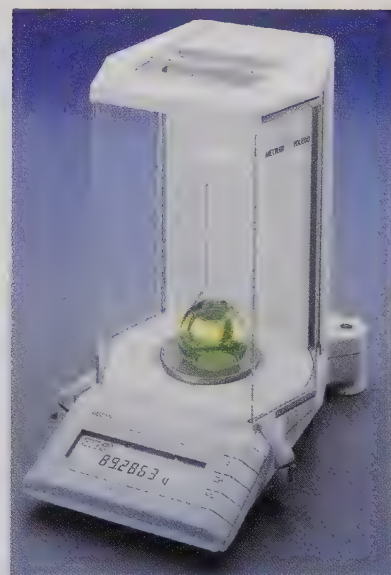
Chemical laboratory work frequently requires measurement of the volumes of liquids. Several devices for the accurate determination of liquid volume are shown in Fig. 1.7.

An important point concerning measurements is the relationship between mass and weight. Although these terms are sometimes used interchangeably, they are *not* the same. **Mass** is a measure of the resistance of an object to a change in its state of motion. Mass is measured by the force necessary to give an object a certain acceleration. On earth we use the force that gravity exerts on an object to measure its mass. We call this force the object's **weight**. Since weight is the response of mass to gravity, it varies with the strength of the gravitational field. Therefore, your body mass is the same on the earth or on the moon, but your weight would be much less on the moon than on earth because of the moon's smaller gravitational field.

Because weighing something on a chemical balance (see Fig. 1.8) involves comparing the mass of that object to a standard mass, the terms *weight* and *mass* are sometimes used interchangeably, although this is incorrect.

**FIGURE 1.7**

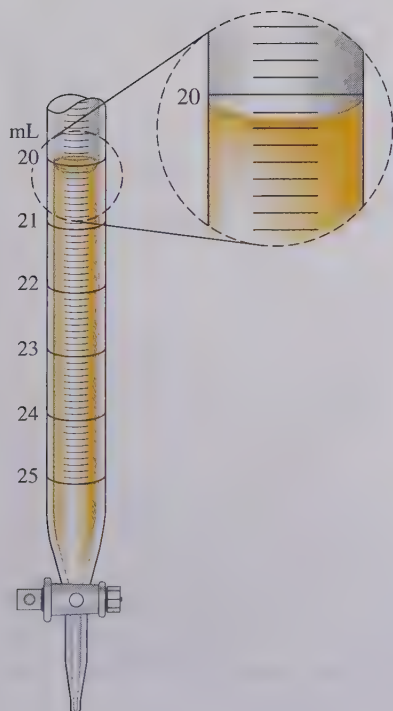
Common types of laboratory equipment used to measure liquid volume.

**FIGURE 1.8**

An electronic analytical balance.

1.4 Uncertainty in Measurement

The number associated with a measurement is obtained using some measuring device. For example, consider the measurement of the volume of a liquid using a buret (shown in Fig. 1.9 with the scale greatly magnified). Notice that the meniscus of the liquid occurs at about 20.15 milliliters. This means that about 20.15 mL of liquid has been delivered from the buret (if the initial position of the liquid meniscus was 0.00 mL). Note that we must estimate the last number of the volume reading by interpolating between the 0.1-mL marks. Since the last number is estimated, its value may be different if another person makes the same measurement. If five different people read the same volume, the results might be as follows:



Person	Results of Measurement
1	20.15 mL
2	20.14 mL
3	20.16 mL
4	20.17 mL
5	20.16 mL

These results show that the first three numbers (20.1) remain the same regardless of who makes the measurement; these are called *certain* digits. However, the digit to the right of the 1 must be estimated and therefore varies; it is called an *uncertain*

FIGURE 1.9

Measurement of volume using a buret. The volume is read at the bottom of the liquid curve (called the *meniscus*).

digit. We customarily report a measurement by recording all the certain digits plus the *first* uncertain digit. In our example it would not make any sense to try to record the volume of thousandths of a milliliter because the value for hundredths of a milliliter must be estimated when using the buret.

It is very important to realize that a *measurement always has some degree of uncertainty*. The uncertainty of a measurement depends on the precision of the measuring device. For example, using a bathroom scale, you might estimate the mass of a grapefruit to be approximately 1.5 pounds. Weighing the same grapefruit on a highly precise balance might produce a result of 1.476 pounds. In the first case, the uncertainty occurs in the tenths of a pound place; in the second case, the uncertainty occurs in the thousandths of a pound place. Suppose we weigh two similar grapefruits on the two devices and obtain the following results:

A measurement always has some degree of uncertainty.

	Bathroom Scale	Balance
Grapefruit 1	1.5 lb	1.476 lb
Grapefruit 2	1.5 lb	1.518 lb

Do the two grapefruits have the same mass? The answer depends on which set of results you consider. Thus a conclusion based on a series of measurements depends on the certainty of those measurements. For this reason, it is important to indicate the uncertainty in any measurement. This is done by always recording the certain digits and the first uncertain digit (the estimated number). These numbers are called the **significant figures** of a measurement.

Uncertainty in measurement is discussed in more detail in Appendix 1.5.

The convention of significant figures automatically indicates something about the uncertainty in a measurement. The uncertainty in the last number (the estimated number) is usually assumed to be ± 1 unless otherwise indicated. For example, the measurement 1.86 kilograms can be taken to mean 1.86 ± 0.01 kilograms.

SAMPLE EXERCISE 1.1

Uncertainty in Measurement

In analyzing a sample of polluted water, a chemist measured out a 25.00-mL water sample with a pipet (see Fig. 1.7). At another point in the analysis, the chemist used a graduated cylinder (see Fig. 1.7) to measure 25 mL of a solution. What is the difference between the measurements 25.00 mL and 25 mL?

SOLUTION

Even though the two volume measurements appear to be equal, they really convey different information. The quantity 25 mL means that the volume is between 24 mL and 26 mL, whereas the quantity 25.00 mL means that the volume is between 24.99 mL and 25.01 mL. The pipet measures volume with much greater precision than does the graduated cylinder.

See Question 1.19.

When making a measurement, it is important to record the results to the appropriate number of significant figures. For example, if a certain buret can be read to ± 0.01 mL, you should record a reading of twenty-five milliliters as 25.00 mL, not 25 mL. This way at some later time when you are using your results to do calculations, the uncertainty in the measurement will be known to you.

Precision and Accuracy

Two terms often used to describe the reliability of measurements are *precision* and *accuracy*. Although these words are frequently used interchangeably in everyday life, they have different meanings in the scientific context. **Accuracy** refers to the agreement of a particular value with the true value. **Precision** refers to the degree of agreement among several measurements of the same quantity. Precision reflects the *reproducibility* of a given type of measurement. The difference between these terms is illustrated by the results of three different dart throws shown in Fig. 1.10.

Two different types of errors are illustrated in Fig. 1.10. A **random error** (also called an *indeterminate error*) means that a measurement has an equal probability of being high or low. This type of error occurs in estimating the value of the last digit of a measurement. The second type of error is called **systematic error** (or *determinate error*). This type of error occurs in the same direction each time; it is either always high or always low. Figure 1.10(a) indicates large random errors (poor technique). Figure 1.10(b) indicates small random errors but a large systematic error, and Figure 1.10(c) indicates small random errors and no systematic error.

In quantitative work, precision is often used as an indication of accuracy; we assume that the *average* of a series of precise measurements (which should “average out” the random errors because of their equal probability of being high or low) is accurate, or close to the “true” value. However, this assumption is valid only if systematic errors are absent. Suppose we weigh a piece of brass five times on a very precise balance and obtain the following results:

Weighing	Result
1	2.486 g
2	2.487 g
3	2.485 g
4	2.484 g
5	2.488 g

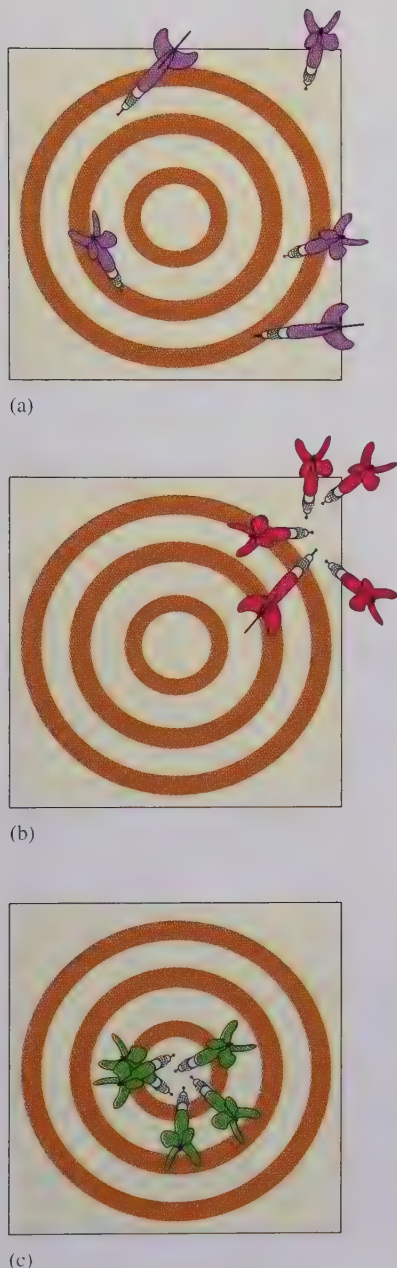
Normally, we would assume that the true mass of the piece of brass is very close to 2.486 grams, which is the average of the five results:

$$\frac{2.486 \text{ g} + 2.487 \text{ g} + 2.485 \text{ g} + 2.484 \text{ g} + 2.488 \text{ g}}{5} = 2.486 \text{ g}$$

However, if the balance has a defect causing it to give a result that is consistently 1.000 gram too high (a systematic error of +1.000 gram), then the measured value of 2.486 grams would be seriously in error. The point here is that high precision among several measurements is an indication of accuracy *only* if systematic errors are absent.

FIGURE 1.10

The results of several dart throws show the difference between *precise* and *accurate*. (a) Neither accurate nor precise (large random errors). (b) Precise but not accurate (small random errors, large systematic error). (c) Bull’s-eye! Both precise and accurate (small random errors, no systematic error).



SAMPLE EXERCISE 1.2

Precision and Accuracy

To check the accuracy of a graduated cylinder, a student filled the cylinder to the 25-mL mark using water delivered from a buret (see Fig. 1.7) and then read the volume delivered. Following are the results of five trials:

Trial	Volume Shown by Graduated Cylinder	Volume Shown by the Buret
1	25 mL	26.54 mL
2	25 mL	26.51 mL
3	25 mL	26.60 mL
4	25 mL	26.49 mL
5	25 mL	26.57 mL
Average	25 mL	26.54 mL

Is the graduated cylinder accurate?

SOLUTION

The results of the trials show very good precision (for a graduated cylinder). The student has good technique. However, note that the average value measured using the buret is significantly different from 25 mL. Thus this graduated cylinder is not very accurate. It produces a systematic error (in this case, the indicated result is low for each measurement).

See Question 1.20.

Precision is an indication of accuracy only if there are no systematic errors.

1.5 Significant Figures and Calculations

Calculating the final result for an experiment usually involves adding, subtracting, multiplying, or dividing the results of various types of measurements. Since it is very important that the uncertainty in the final result is known correctly, we have developed rules for counting the significant figures in each number and for determining the correct number of significant figures in the final result.

Rules for Counting Significant Figures

1. **Nonzero integers.** Nonzero integers always count as significant figures.
2. **Zeros.** There are three classes of zeros:
 - a. **Leading zeros** are zeros that precede all the nonzero digits. These do not count as significant figures. In the number 0.0025, the three zeros simply indicate the position of the decimal point. This number has only two significant figures.
 - b. **Captive zeros** are zeros between nonzero digits. These always count as significant figures. The number 1.008 has four significant figures.

Leading zeros are never significant figures.

Captive zeros are always significant figures.

Trailing zeros are sometimes significant figures.

Exact numbers never limit the number of significant figures in a calculation.

Exponential notation is reviewed in Appendix 1.1.

c. *Trailing zeros* are zeros at the *right end* of the number. They are significant only if the number contains a decimal point. The number 100 has only one significant figure, whereas the number 1.00×10^2 has three significant figures. The number one hundred written as 100. also has three significant figures.

3. *Exact numbers.* Many times calculations involve numbers that were not obtained using measuring devices but were determined by counting: 10 experiments, 3 apples, 8 molecules. Such numbers are called *exact numbers*. They can be assumed to have an infinite number of significant figures. Other examples of exact numbers are the 2 in $2\pi r$ (the circumference of a circle) and the 4 and the 3 in $\frac{4}{3}\pi r^3$ (the volume of a sphere). Exact numbers also can arise from definitions. For example, one inch is defined as *exactly* 2.54 centimeters. Thus, in the statement $1 \text{ in} = 2.54 \text{ cm}$, neither the 2.54 nor the 1 limits the number of significant figures when used in a calculation.

Note that the number 1.00×10^2 above is written in **exponential notation**. This type of notation has at least two advantages: the number of significant figures can be easily indicated, and fewer zeros are needed to write a very large or very small number. For example, the number 0.000060 is much more conveniently represented as 6.0×10^{-5} . (The number has two significant figures.)

SAMPLE EXERCISE 1.3

Significant Figures

Give the number of significant figures for each of the following results.

- A student's extraction procedure on tea yields 0.0105 g of caffeine.
- A chemist records a mass of 0.050080 g in an analysis.
- In an experiment a span of time is determined to be $8.050 \times 10^{-3} \text{ s}$.

SOLUTION

- The number contains three significant figures. The zeros to the left of the 1 are leading zeros and are not significant, but the remaining zero (a captive zero) is significant.
- The number contains five significant figures. The leading zeros (to the left of the 5) are not significant. The captive zeros between the 5 and the 8 are significant, and the trailing zero to the right of the 8 is significant because the number contains a decimal point.
- This number has four significant figures. Both zeros are significant.

See Exercises 1.25 and 1.26.



Caffeine, which occurs in such items as tea, coffee, and cola nuts, is a respiratory and cardiac stimulant.

To this point we have learned to count the significant figures in a given number. Next, we must consider how uncertainty accumulates as calculations are carried out. The detailed analysis of the accumulation of uncertainties depends on the type of calculation involved and can be complex. However, in this textbook we will employ the following simple rules that have been developed for determining the appropriate number of significant figures in the result of a calculation.

1. For multiplication or division, the number of significant figures in the result is the same as the number in the least precise measurement used in the calculation. For example, consider the calculation

$4.56 \times 1.4 = 6.38$ $\xrightarrow{\text{Corrected}}$ **6.4**

Limiting term has two significant figures

Two significant figures

2. For addition or subtraction, the result has the same number of decimal places as the least precise measurement used in the calculation. For example, consider the sum

12.11
18.0 ← Limiting term has one decimal place
1.013
31.123 → **31.1**
 ↑
 One decimal place

Note that for multiplication and division, significant figures are counted. For addition and subtraction, the decimal places are counted.

In most calculations you will need to round numbers to obtain the correct number of significant figures. The following rules should be applied when rounding.

1. In a series of calculations, carry the extra digits through to the final result, *then* round.

2. If the digit to be removed
 - a. is less than 5, the preceding digit stays the same. For example, 1.33 rounds to 1.3.
 - b. is equal to or greater than 5, the preceding digit is increased by 1. For example, 1.36 rounds to 1.4.

Although rounding is generally straightforward, one point requires special emphasis. As an illustration, suppose that the number 4.348 needs to be rounded to two significant figures. In doing this, we look *only* at the *first number* to the right of the 3:

4.348

↑

Look at this number to round to two significant figures.

*Although these simple rules work well for most cases, they can give misleading results in certain cases. For more information, see L. M. Schwartz, "Propagation of Significant Figures," *J. Chem. Ed.* **62** (1985): 693; and H. Bradford Thompson, "Is 8°C equal to 50°F?" *J. Chem. Ed.* **68** (1991): 400.

Rule 2 is consistent with the operation of electronic calculators.

Do not round sequentially. The number 6.8347 rounded to three significant figures is 6.83, not 6.84.

The number is rounded to 4.3 because 4 is less than 5. It is incorrect to round sequentially. For example, do *not* round the 4 to 5 to give 4.35 and then round the 3 to 4 to give 4.4.

When rounding, *use only the first number to the right of the last significant figure.*

It is important to note that Rule 1 above usually will not be followed in the Sample Exercises in this text because we want to show the correct number of significant figures in *each step* of a problem. This same practice is followed for the detailed solutions given in the *Solutions Guide*. However, as stated in Rule 1, the best procedure is to carry extra digits throughout a series of calculations and round to the correct number of significant figures only at the end. This is the practice you should follow. The fact that your rounding procedures are different from those used in this text must be taken into account when you check your answer with the one given at the end of the book or in the *Solutions Guide*. Your answer (based on rounding only at the end of a calculation) may differ in the last place from that given here as the “correct” answer because we have rounded after each step. To help you understand the difference between these rounding procedures, we will consider them further in Sample Exercise 1.4.

SAMPLE EXERCISE 1.4

Significant Figures in Mathematical Operations

Carry out the following mathematical operations, and give each result with the correct number of significant figures.

- $1.05 \times 10^{-3} \div 6.135$
- $21 - 13.8$
- As part of a lab assignment to determine the value of the gas constant (R), a student measured the pressure (P), volume (V), and temperature (T) for a sample of gas, where

$$R = \frac{PV}{T}$$

The following values were obtained: $P = 2.560$, $T = 275.15$, and $V = 8.8$. (Gases will be discussed in detail in Chapter 5; we will not be concerned at this time about the units for these quantities.) Calculate R to the correct number of significant figures.

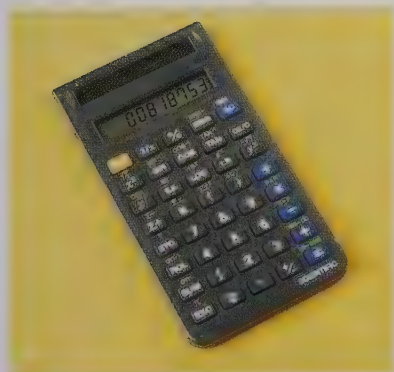
SOLUTION

- The result is 1.71×10^{-4} , which has three significant figures because the term with the least precision (1.05×10^{-3}) has three significant figures.
- The result is 7 with no decimal place because the number with the least number of decimal places (21) has none.

$$c. \quad R = \frac{PV}{T} = \frac{(2.560)(8.8)}{275.15}$$

The correct procedure for obtaining the final result can be represented as follows:

$$\begin{aligned} \frac{(2.560)(8.8)}{275.15} &= \frac{22.528}{275.15} = 0.0818753 \\ &= 0.082 = 8.2 \times 10^{-2} = R \end{aligned}$$



This number must be rounded to two significant figures.

The final result must be rounded to two significant figures because 8.8 (the least precise measurement) has two significant figures. To show the effects of rounding at intermediate steps, we will carry out the calculation as follows:

$$\begin{array}{c} \text{Rounded to two} \\ \text{significant figures} \\ \downarrow \\ \frac{(2.560)(8.8)}{275.15} = \frac{22.528}{275.15} = \frac{23}{275.15} \end{array}$$

Now we proceed with the next calculation:

$$\frac{23}{275.15} = 0.0835908$$

Rounded to two significant figures, this result is

$$0.084 = 8.4 \times 10^{-2}$$

Note that intermediate rounding gives a significantly different result than was obtained by rounding only at the end. Again, we must reemphasize that in *your* calculations you should round *only at the end*. However, because rounding is carried out at intermediate steps in this text (to always show the correct number of significant figures), the final answer given in the text may differ slightly from the one you obtain (rounding only at the end).

See Exercises 1.29 through 1.32.

There is a useful lesson to be learned from part c of Sample Exercise 1.4. The student measured the pressure and temperature to greater precision than the volume. A more precise value of R (one with more significant figures) could have been obtained if a more precise measurement of V had been made. As it is, the efforts expended to measure P and T very precisely were wasted. Remember that a series of measurements to obtain some final result should all be done to about the same precision.

1.6 Dimensional Analysis

It is often necessary to convert a given result from one system of units to another. The best way to do this is by a method called the **unit factor method**, or more commonly **dimensional analysis**. To illustrate the use of this method, we will consider several unit conversions. Some equivalents in the English and metric systems are listed in Table 1.4. A more complete list of conversion factors given to more significant figures appears in Appendix 6.

Consider a pin measuring 2.85 centimeters in length. What is its length in inches? To accomplish this conversion, we must use the equivalence statement

$$2.54 \text{ cm} = 1 \text{ in}$$

If we divide both sides of this equation by 2.54 centimeters, we get

$$\frac{2.54 \text{ cm}}{2.54 \text{ cm}} = 1 = \frac{1 \text{ in}}{2.54 \text{ cm}}$$

TABLE 1.4
English–Metric Equivalents

Length	1 m = 1.094 yd 2.54 cm = 1 in
Mass	1 kg = 2.205 lb 453.6 g = 1 lb
Volume	1 L = 1.06 qt 1 ft ³ = 28.32 L

Note that the expression $1 \text{ in}/2.54 \text{ cm}$ equals 1. This expression is called a *unit factor*. Since 1 inch and 2.54 centimeters are exactly equivalent, multiplying any expression by this unit factor will not change its *value*.

The pin has a length of 2.85 centimeters. Multiplying this length by the appropriate unit factor gives

$$2.85 \text{ cm} \times \frac{1 \text{ in}}{2.54 \text{ cm}} = \frac{2.85}{2.54} \text{ in} = 1.12 \text{ in}$$

Note that the centimeter units cancel to give inches for the result. This is exactly what we wanted to accomplish. Note also that the result has three significant figures, as required by the number 2.85. Recall that the 1 and 2.54 in the conversion factor are exact numbers by definition.

SAMPLE EXERCISE 1.5

Unit Conversions I

A pencil is 7.00 in long. What is its length in centimeters?

SOLUTION

In this case we want to convert from inches to centimeters. Therefore, we must use the reciprocal of the unit factor used above to do the opposite conversion:

$$7.00 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = (7.00)(2.54) \text{ cm} = 17.8 \text{ cm}$$

Here the inch units cancel, leaving centimeters, as requested.

See Exercises 1.35 and 1.36.

Note that two unit factors can be derived from each equivalence statement. For example, from the equivalence statement $2.54 \text{ cm} = 1 \text{ in}$, the two unit factors are

$$\frac{2.54 \text{ cm}}{1 \text{ in}} \quad \text{and} \quad \frac{1 \text{ in}}{2.54 \text{ cm}}$$

How do you choose which one to use in a given situation? Simply look at the *direction* of the required change. To change from inches to centimeters, the inches must cancel. Thus the factor $2.54 \text{ cm}/1 \text{ in}$ is used. To change from centimeters to inches, centimeters must cancel, and the factor $1 \text{ in}/2.54 \text{ cm}$ is appropriate.

Consider the direction of the required change to select the correct unit factor.

Converting from One Unit to Another

- To convert from one unit to another, use the equivalence statement that relates the two units.
- Derive the appropriate unit factor by looking at the direction of the required change (to cancel the unwanted units).
- Multiply the quantity to be converted by the unit factor to give the quantity with the desired units.

SAMPLE EXERCISE 1.6

Unit Conversions II

You want to order a bicycle with a 25.5-in frame, but the sizes in the catalog are given only in centimeters. What size should you order?

SOLUTION

You need to go from inches to centimeters, so $2.54 \text{ cm} = 1 \text{ in}$ is appropriate:

$$25.5 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 64.8 \text{ cm}$$

See Exercises 1.35 and 1.36.

To ensure that the conversion procedure is clear, a multistep problem is considered in Sample Exercise 1.7.

SAMPLE EXERCISE 1.7

Unit Conversions III

A student has entered a 10.0-km run. How long is the run in miles?

SOLUTION

This conversion can be accomplished in several different ways. Since we have the equivalence statement $1 \text{ m} = 1.094 \text{ yd}$, we will proceed by a path that uses this fact. Before we start any calculations, let us consider our strategy. We have kilometers, which we want to change to miles. We can do this by the following route:

kilometers $\longrightarrow$ meters $\longrightarrow$ yards $\longrightarrow$ miles

To proceed in this way, we need the following equivalence statements:

$$1 \text{ km} = 1000 \text{ m}$$

$$1 \text{ m} = 1.094 \text{ yd}$$

$$1760 \text{ yd} = 1 \text{ mi}$$

To make sure the process is clear, we will proceed step by step:

KILOMETERS TO METERS:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} = 1.00 \times 10^4 \text{ m}$$

METERS TO YARDS:

$$1.00 \times 10^4 \text{ m} \times \frac{1.094 \text{ yd}}{1 \text{ m}} = 1.094 \times 10^4 \text{ yd}$$

Note that we should have only three significant figures in the result. Since this is an intermediate result, however, we will carry the extra digit. Remember, round off only the final result.

YARDS TO MILES:

$$1.094 \times 10^4 \text{ yd} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.216 \text{ mi}$$

Normally we round to the correct number of significant figures after each step. However, you should round only at the end.

Note in this case that 1 mi equals exactly 1760 yd by *designation*. Thus 1760 is an exact number.

Since the distance was originally given as 10.0 km, the result can have only three significant figures and should be rounded to 6.22 mi. Thus

$$10.0 \text{ km} = 6.22 \text{ mi}$$

Alternatively, we can combine the steps:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1.094 \text{ yd}}{1 \text{ m}} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.22 \text{ mi}$$

See Exercises 1.35 and 1.36.

In using dimensional analysis, your verification that everything has been done correctly is that you end up with the correct units. *In doing chemistry problems, you should always include the units for the quantities used.* Always check to see that the units cancel to give the correct units for the final result. This provides a very valuable check, especially for complicated problems.

Study the procedures for unit conversions in the following Sample Exercises.

SAMPLE EXERCISE 1.8

Unit Conversion IV

The speed limit on many highways in the United States is 55 mi/h. What number would be posted in kilometers per hour?

SOLUTION

Result obtained by
rounding only at the
end of the calculation

$$\frac{55 \text{ mi}}{\text{h}} \times \frac{1760 \text{ yd}}{1 \text{ mi}} \times \frac{1 \text{ m}}{1.094 \text{ yd}} \times \frac{1 \text{ km}}{1000 \text{ m}} = 88 \text{ km/h}$$

Note that all units cancel except the desired kilometers per hour.

See Exercises 1.41 and 1.42.

SAMPLE EXERCISE 1.9

Unit Conversions V

A Japanese car is advertised as having a gas mileage of 15 km/L. Convert this rating to miles per gallon.

SOLUTION

Result obtained by
rounding only at the
end of the calculation

$$\frac{15 \text{ km}}{\text{L}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1.094 \text{ yd}}{1 \text{ m}} \times \frac{1 \text{ mi}}{1760 \text{ yd}} \times \frac{1 \text{ L}}{1.06 \text{ qt}} \times \frac{4 \text{ qt}}{1 \text{ gal}} = 35 \text{ mi/gal}$$

See Exercises 1.43 and 1.44.

1.7 Temperature

Three systems for measuring temperature are widely used: the Celsius scale, the Kelvin scale, and the Fahrenheit scale. The first two temperature systems are used in the physical sciences, and the third is used in many of the engineering sciences. Our purpose here is to define the three temperature scales and show how conversions from one scale to another can be performed. Although these conversions can be carried out routinely on most calculators, we will consider the process in some detail here to illustrate methods of problem solving.

The three temperature scales are defined and compared in Fig. 1.11. Note that the size of the temperature unit (the *degree*) is the same for the Kelvin and Celsius scales. The fundamental difference between these two temperature scales is in their zero points. Conversion between these two scales simply requires an adjustment for the different zero points.

$$T_K = T_C + 273.15$$

$$\text{Temperature (Kelvin)} = \text{temperature (Celsius)} + 273.15$$

or

$$T_C = T_K - 273.15$$

$$\text{Temperature (Celsius)} = \text{temperature (Kelvin)} - 273.15$$

For example, to convert 300.00 K to the Celsius scale, we do the following calculation:

$$300.00 - 273.15 = 26.85^\circ\text{C}$$

Note that in expressing temperature in Celsius units, the designation $^\circ\text{C}$ is used. The degree symbol is not used when writing temperature in terms of the Kelvin scale. The unit of temperature on this scale is called a *kelvin* and is symbolized by the letter K.

Converting between the Fahrenheit and Celsius scales is somewhat more complicated because both the degree sizes and the zero points are different. Thus we

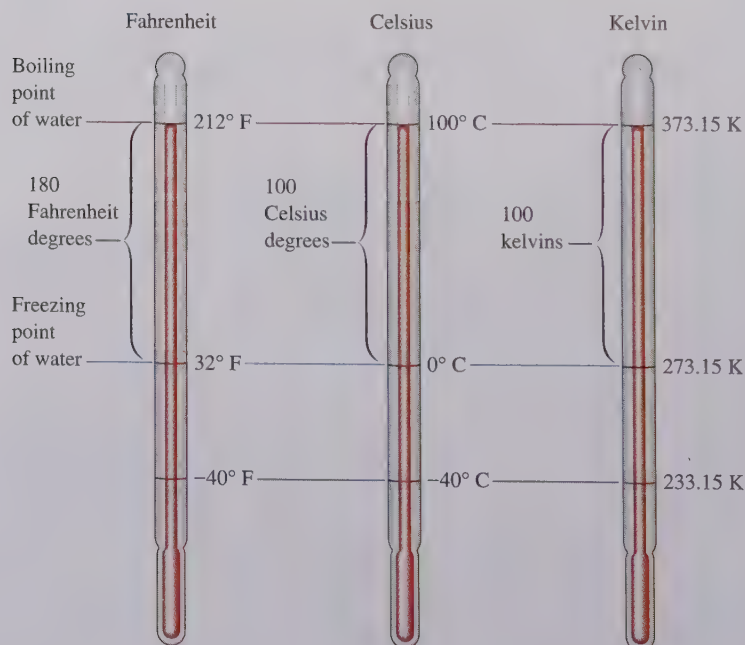


FIGURE 1.11
The three major temperature scales.

need to consider two adjustments: one for degree size and one for the zero point. First, we must account for the difference in degree size. This can be done by re-considering Fig. 1.11. Notice that since $212^{\circ}\text{F} = 100^{\circ}\text{C}$ and $32^{\circ}\text{F} = 0^{\circ}\text{C}$,

$$212 - 32 = 180 \text{ Fahrenheit degrees} = 100 - 0 = 100 \text{ Celsius degrees}$$

Thus 180° on the Fahrenheit scale is equivalent to 100° on the Celsius scale, and the unit factor is

$$\frac{180^{\circ}\text{F}}{100^{\circ}\text{C}} \quad \text{or} \quad \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}}$$

or the reciprocal, depending on the direction in which we need to go.

Next, we must consider the different zero points. Since $32^{\circ}\text{F} = 0^{\circ}\text{C}$, we obtain the corresponding Celsius temperature by first subtracting 32 from the Fahrenheit temperature to account for the different zero points. Then the unit factor is applied to adjust for the difference in the degree size. This process is summarized by the equation

$$(T_{\text{F}} - 32^{\circ}\text{F}) \frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} = T_{\text{C}} \quad (1.1)$$

where T_{F} and T_{C} represent a given temperature on the Fahrenheit and Celsius scales, respectively. In the opposite conversion, we first correct for degree size and then correct for the different zero point. This process can be summarized in the following general equation:

$$T_{\text{F}} = T_{\text{C}} \times \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}} + 32^{\circ}\text{F} \quad (1.2)$$

Equations (1.1) and (1.2) are really the same equation in different forms. See if you can obtain Equation (1.2) by starting with Equation (1.1) and rearranging.

At this point it is worthwhile to weigh the two alternatives for learning to do temperature conversions: You can simply memorize the equations, or you can take the time to learn the differences between the temperature scales and to understand the processes involved in converting from one scale to another. The latter approach may take a little more effort, but the understanding you gain will stick with you much longer than the memorized formulas. This choice also will apply to many of the other chemical concepts. Try to think things through!

Understand the process of converting from one temperature scale to another; do not simply memorize the equations.

SAMPLE EXERCISE 1.10



A physician taking the temperature of a patient.

Temperature Conversions I

Normal body temperature is 98.6°F . Convert this temperature to the Celsius and Kelvin scales.

SOLUTION

Rather than simply using the formulas to solve this problem, we will proceed by thinking it through. The situation is diagramed in Fig. 1.12. First, we want to convert 98.6°F to the Celsius scale. The number of Fahrenheit degrees between 32.0°F and 98.6°F is 66.6°F . We must convert this difference to Celsius degrees:

$$66.6^{\circ}\text{F} \times \frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} = 37.0^{\circ}\text{C}$$

Thus 98.6°F corresponds to 37.0°C .

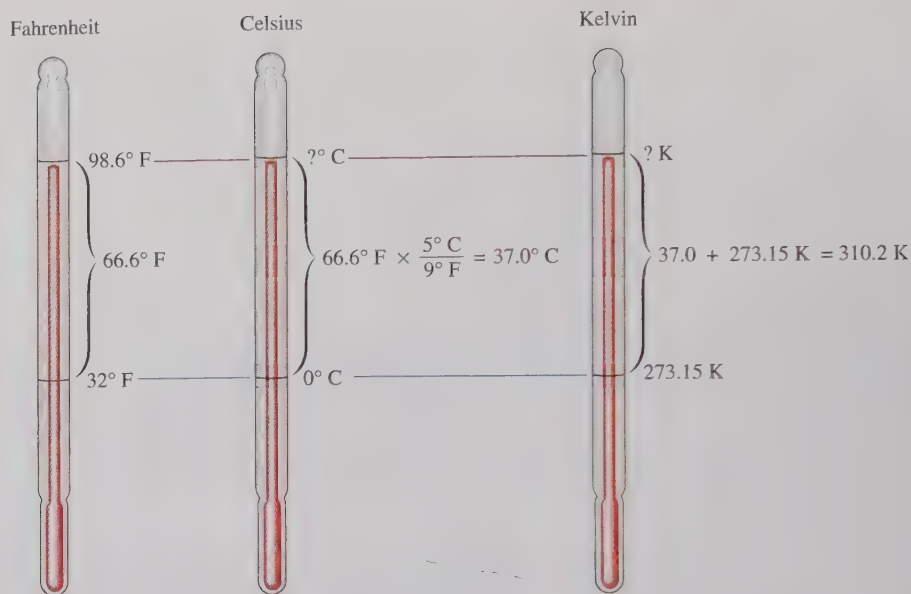


FIGURE 1.12
Normal body temperature on the Fahrenheit, Celsius, and Kelvin scales.

Now we can convert to the Kelvin scale:

$$T_K = T_C + 273.15 = 37.0 + 273.15 = 310.2\text{ K}$$

Note that the final answer has only one decimal place (37.0 is limiting).

See Exercises 1.47 and 1.48.

SAMPLE EXERCISE 1.11

Temperature Conversions II

One interesting feature of the Celsius and Fahrenheit scales is that -40°C and -40°F represent the same temperature, as shown in Fig. 1.11. Verify that this is true.

SOLUTION

The difference between 32°F and -40°F is 72°F . The difference between 0°C and -40°C is 40°C . The ratio of these is

$$\frac{72^\circ\text{F}}{40^\circ\text{C}} = \frac{8 \times 9^\circ\text{F}}{8 \times 5^\circ\text{C}} = \frac{9^\circ\text{F}}{5^\circ\text{C}}$$

as required. Thus -40°C is equivalent to -40°F .

See Challenge Problem 1.84.

Since, as shown in Sample Exercise 1.11, -40° on both the Fahrenheit and Celsius scales represents the same temperature, this point can be used as a reference point (like 0°C and 32°F) for a relationship between the two scales:

$$\frac{\text{Number of Fahrenheit degrees}}{\text{Number of Celsius degrees}} = \frac{T_F - (-40)}{T_C - (-40)} = \frac{9^\circ\text{F}}{5^\circ\text{C}}$$

or

$$\frac{T_F + 40}{T_C + 40} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \quad (1.3)$$

where T_F and T_C represent the same temperature (but not the same number). This equation can be used to convert Fahrenheit temperatures to Celsius and vice versa and may be easier to remember than Equations (1.1) and (1.2).

SAMPLE EXERCISE 1.12

Temperature Conversions III

Liquid nitrogen, which is often used as a coolant for low-temperature experiments, has a boiling point of 77 K. What is this temperature on the Fahrenheit scale?

SOLUTION

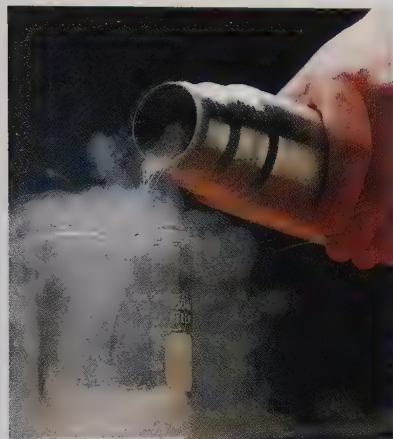
We will first convert 77 K to the Celsius scale:

$$T_C = T_K - 273.15 = 77 - 273.15 = -196^\circ\text{C}$$

To convert to the Fahrenheit scale, we will use Equation (1.3):

$$\begin{aligned}\frac{T_F + 40}{T_C + 40} &= \frac{9^\circ\text{F}}{5^\circ\text{C}} \\ \frac{T_F + 40}{-196^\circ\text{C} + 40} &= \frac{T_F + 40}{-156^\circ\text{C}} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \\ T_F + 40 &= \frac{9^\circ\text{F}}{5^\circ\text{C}}(-156^\circ\text{C}) = -281^\circ\text{F} \\ T_F &= -281^\circ\text{F} - 40 = -321^\circ\text{F}\end{aligned}$$

See Exercises 1.49 and 1.50.



Liquid nitrogen is so cold that water condenses out of the surrounding air, forming a cloud as the nitrogen is poured.

1.8 Density

A property of matter that is often used by chemists as an “identification tag” for a substance is **density**, the mass of substance per unit volume of the substance:

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

The density of a liquid can be determined easily by weighing an accurately known volume of liquid. This procedure is illustrated in Sample Exercise 1.13.

SAMPLE EXERCISE 1.13

Determining Density

A chemist, trying to identify the main component of a compact disc cleaning fluid, finds that 25.00 cm^3 of the substance has a mass of 19.625 g at 20°C . The following are the names and densities of the compounds that might be the main component:

Compound	Density in g/cm^3 at 20°C
Chloroform	1.492
Diethyl ether	0.714
Ethanol	0.789
Isopropyl alcohol	0.785
Toluene	0.867

There are two ways of indicating units that occur in the denominator. For example, we can write g/cm^3 or g cm^{-3} . Although we will use the former system here, the other system is widely used.

Which of these compounds is the most likely to be the main component of the compact disc cleaner?

SOLUTION

To identify the unknown substance, we must determine its density. This can be done by using the definition of density:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{19.625 \text{ g}}{25.00 \text{ cm}^3} = 0.7850 \text{ g/cm}^3$$

This density corresponds exactly to that of isopropyl alcohol, which is therefore the most likely main component of the cleaner. However, note that the density of ethanol is also very close. To be sure that the compound is isopropyl alcohol, we should run several more density experiments. (In the modern laboratory, many other types of tests could be done to distinguish between these two liquids.)

See Exercises 1.55 and 1.56.

Besides being a tool for the identification of substances, density has many other uses. For example, the liquid in your car's lead storage battery (a solution of sulfuric acid) changes density because the sulfuric acid is consumed as the battery discharges. In a fully charged battery, the density of the solution is about 1.30 g/cm^3 . If the density falls below 1.20 g/cm^3 , the battery will have to be recharged. Density measurement is also used to determine the amount of antifreeze, and thus the level of protection against freezing, in the cooling system of a car.

The densities of various common substances are given in Table 1.5.

1.9 Classification of Matter

Before we can hope to understand the changes we see going on around us—the growth of plants, the rusting of steel, the aging of people, rain becoming more acidic—we must find out how matter is organized. **Matter**, best defined as anything occupying space and having mass, is the material of the universe. Matter is com-

TABLE 1.5 Densities of Various Common Substances* at 20°C

Substance	Physical State	Density (g/cm^3)
Oxygen	Gas	0.00133
Hydrogen	Gas	0.000084
Ethanol	Liquid	0.789
Benzene	Liquid	0.880
Water	Liquid	0.9982
Magnesium	Solid	1.74
Salt (sodium chloride)	Solid	2.16
Aluminum	Solid	2.70
Iron	Solid	7.87
Copper	Solid	8.96
Silver	Solid	10.5
Lead	Solid	11.34
Mercury	Liquid	13.6
Gold	Solid	19.32

*At 1 atmosphere pressure

plex and has many levels of organization. In this section we introduce basic ideas about the structure of matter and its behavior.

We will start by considering the definitions of the fundamental properties of matter. Matter exists in three **states**: solid, liquid, and gas. A *solid* is rigid; it has a fixed volume and shape. A *liquid* has a definite volume but no specific shape; it assumes the shape of its container. A *gas* has no fixed volume or shape; it takes on the shape and volume of its container. In contrast to liquids and solids, which are only slightly compressible, gases are highly compressible; it is relatively easy to decrease the volume of a gas. Molecular-level pictures of the three states of water are given in Fig. 1.13. The different properties of ice, liquid water, and steam are determined by the different arrangements of the molecules in these substances. Table 1.5 gives the states of some common substances at 20°C and 1 atmosphere of pressure.

Most of the matter around us consists of **mixtures** of pure substances. Wood, gasoline, wine, soil, and air are all mixtures. The main characteristic of a mixture is that it has *variable composition*. For example, wood is a mixture of many substances, the proportions of which vary depending on the type of wood and where it grows. Mixtures can be classified as **homogeneous** (having visibly indistinguishable parts) or **heterogeneous** (having visibly distinguishable parts).

A homogeneous mixture is called a **solution**. Air is a solution consisting of a mixture of gases. Wine is a complex liquid solution. Brass is a solid solution of copper and zinc. Sand in water and iced tea with ice cubes are examples of heterogeneous mixtures. Heterogeneous mixtures usually can be separated into two or more homogeneous mixtures or pure substances (for example, the ice cubes can be separated from the tea).

Mixtures can be separated into pure substances by physical methods. A **pure substance** is one with constant composition. Water is a good illustration of these ideas. As we will discuss in detail later, pure water is composed solely of H_2O molecules, but the water found in nature (groundwater or the water in a lake or ocean)

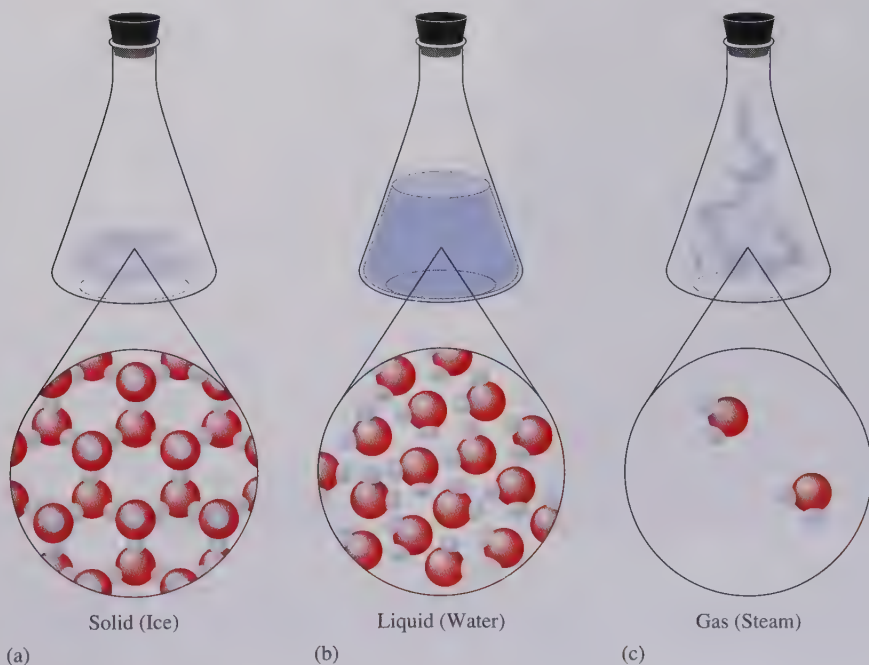


FIGURE 1.13

The three states of water (where red spheres represent oxygen atoms and blue spheres represent hydrogen atoms). (a) Solid: the water molecules are locked into rigid positions and are close together. (b) Liquid: the water molecules are still close together but can move around to some extent. (c) Gas: the water molecules are far apart and move randomly.

is really a mixture. Seawater, for example, contains large amounts of dissolved minerals. Boiling seawater produces steam, which can be condensed to pure water, leaving the minerals behind as solids. The dissolved minerals in seawater also can be separated out by freezing the mixture, since pure water freezes out. The processes of boiling and freezing cause **physical changes**: When water freezes or boils, it changes its state but remains water; it is still composed of H_2O molecules. A physical change is a change in the form of a substance, not in its chemical composition. A physical change can be used to separate a mixture into pure compounds, but it will not break compounds into elements.

One of the most important methods for separating the components of a mixture is **distillation**, a process that depends on differences in the volatility (how readily substances become gases) of the components. In simple distillation, a mixture is heated in a device such as that shown in Fig. 1.14. The most volatile component vaporizes at the lowest temperature, and the vapor passes through a cooled tube (a condenser), where it condenses back into its liquid state.

The simple, one-stage distillation apparatus shown in Fig. 1.14 works very well when only one component of the mixture is volatile. For example, a mixture of water and sand is easily separated by boiling off the water. Water containing dissolved minerals behaves in much the same way. As the water is boiled off, the minerals remain behind as nonvolatile solids. Simple distillation of seawater using the sun as the heat source is an excellent way to desalinate (remove the minerals from) seawater.

The term *volatile* refers to the ease with which a substance can be changed to its vapor.

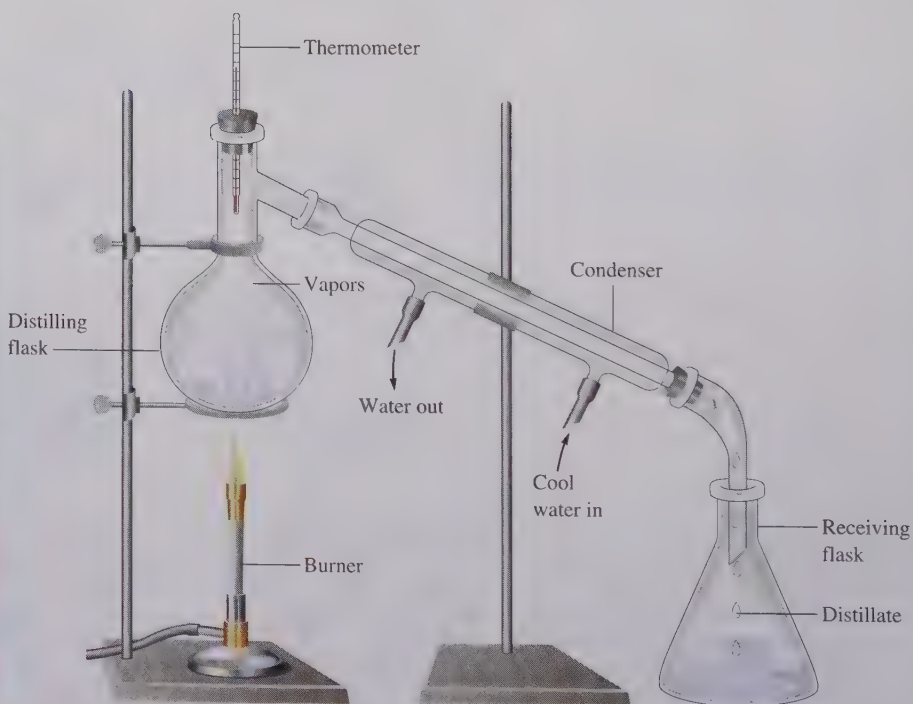
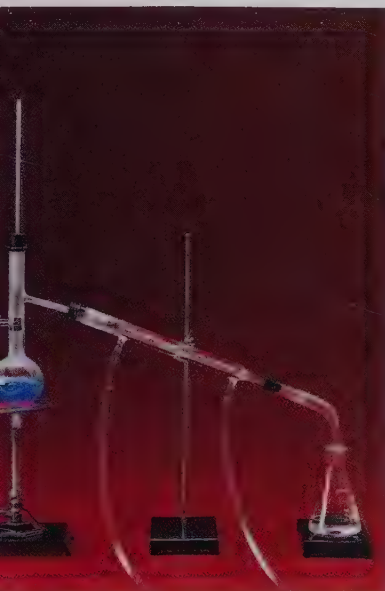
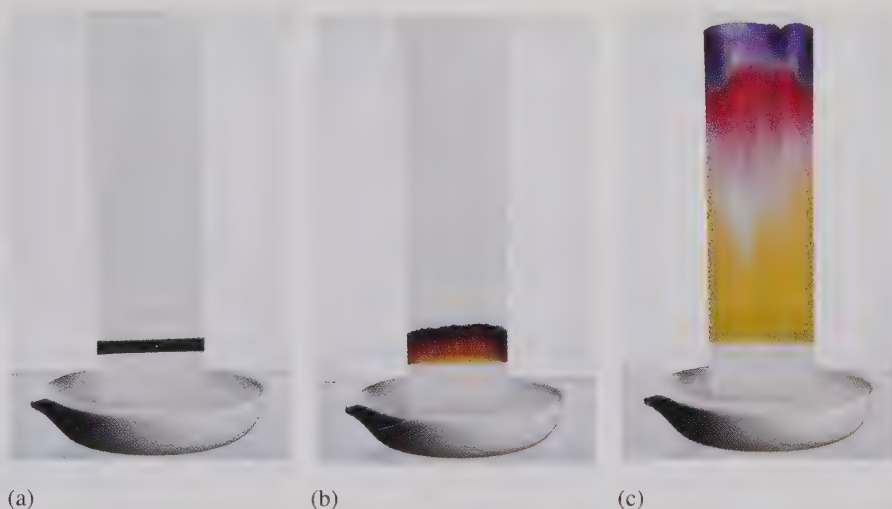


FIGURE 1.14
Simple laboratory distillation apparatus. Cool water circulates through the outer portion of the condenser, causing vapors from the distilling flask to condense into a liquid. The nonvolatile component of the mixture remains in the distilling flask.

FIGURE 1.15

Paper chromatography of ink. (a) A line of the mixture to be separated is placed at one end of a sheet of porous paper. (b) The paper acts as a wick to draw up the liquid. (c) The component with the weakest attraction for the paper travels faster than the components that cling to the paper.



However, when a mixture contains several volatile components, the one-step distillation does not give a pure substance in the receiving flask, and more elaborate methods are required.

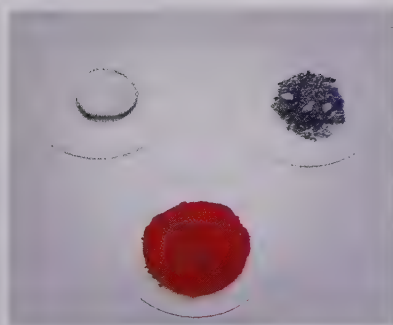
Another method of separation is simple **filtration**, which is used when a mixture consists of a solid and a liquid. The mixture is poured onto a mesh, such as filter paper, which passes the liquid and leaves the solid behind.

A third method of separation is called **chromatography**. Chromatography is the general name applied to a series of methods that employ a system with two *phases* (states) of matter: a mobile phase and a stationary phase. The *stationary phase* is a solid, and the *mobile phase* is either a liquid or a gas. The separation process occurs because the components of the mixture have different affinities for the two phases and thus move through the system at different rates. A component with a high affinity for the mobile phase moves relatively quickly through the chromatographic system, whereas one with a high affinity for the solid phase moves more slowly.

One simple type of chromatography, **paper chromatography**, employs a strip of porous paper, such as filter paper, for the stationary phase. A drop of the mixture to be separated is placed on the paper, which is then dipped into a liquid (the mobile phase) that travels up the paper as though it were a wick (see Fig. 1.15). This method of separating a mixture is often used by biochemists, who study the chemistry of living systems.

It should be noted that when a mixture is separated, the absolute purity of the separated components is an ideal. Because water, for example, inevitably comes into contact with other materials when it is synthesized or separated from a mixture, it is never absolutely pure. With great care, however, substances can be obtained in very nearly pure form.

Pure substances contain compounds (combinations of elements) or free elements. A **compound** is a substance with *constant composition* that can be broken down into elements by chemical processes. An example of a chemical process is the electrolysis of water, in which an electric current is passed through water to break it down into the free elements hydrogen and oxygen. This process produces a chemical change because the water molecules have been broken down. The water is gone, and in its place we have the free elements hydrogen and oxygen. A **chemical change**



The element mercury (top left) combines with the element iodine (top right) to form the compound mercuric iodide (bottom). This is an example of a chemical change.

is one in which a given substance becomes a new substance or substances with different properties and different composition. **Elements** are substances that cannot be decomposed into simpler substances by chemical or physical means.

We have seen that the matter around us has various levels of organization. The most fundamental substances we have discussed so far are elements. As we will see in later chapters, elements also have structure: They are composed of atoms, which in turn are composed of nuclei and electrons. Even the nucleus has structure: it is composed of protons and neutrons. And even these can be broken down further, into elementary particles called *quarks*. However, we need not concern ourselves with such details at this point. Figure 1.16 summarizes our discussion of the organization of matter.

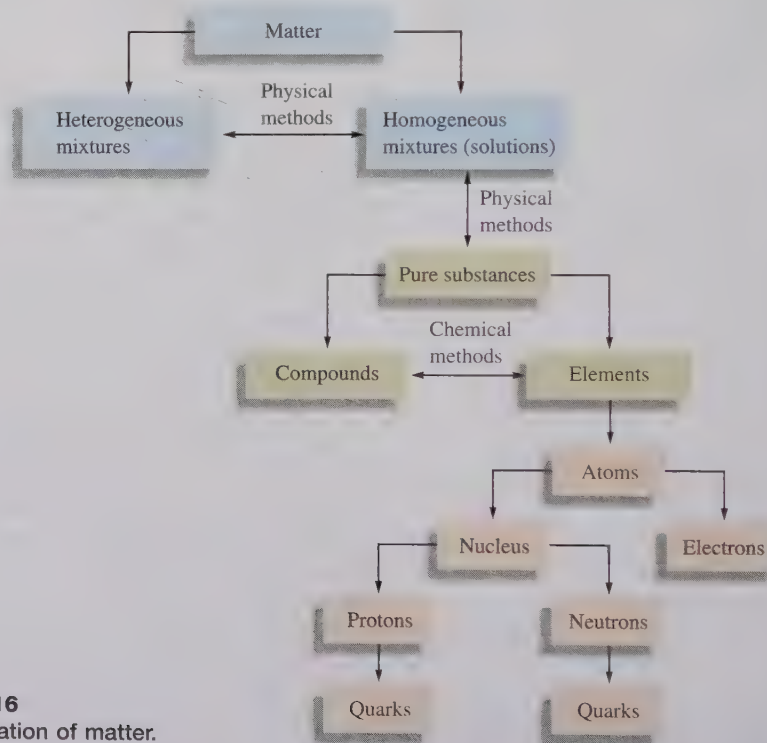


FIGURE 1.16
The organization of matter.

For Review

Summary

Ideally, the progress of any science occurs by use of the scientific method, which first makes observations of nature and then looks for patterns in the observations that often lead to the formulation of natural laws. A theory or model is then constructed to provide an interpretation of the behavior of nature. The theory is tested by further experiments and is modified as necessary.

Key Terms

Section 1.2

scientific method
measurement
hypothesis
theory
model
natural law
law of conservation of mass

Section 1.3

SI system
mass
weight

Section 1.4

uncertainty
significant figures
accuracy
precision

random error
systematic error

Section 1.5

exponential notation

Section 1.6

unit factor method
dimensional analysis

Section 1.8

density

Section 1.9

matter
states (of matter)
homogeneous mixture
heterogeneous mixture
solution
pure substance
physical change
distillation
filtration
chromatography
paper chromatography
compound
chemical change
element

Quantitative observations are called measurements and always consist of a number and a scale or unit. Measurement always involves some uncertainty. Drawing conclusions from the results of measurements requires that the extent of the uncertainty be known. This information is conveyed by using the correct number of significant figures. The preferred system of units among scientists is the SI system. Converting results from one set of units to another is accomplished with unit factors (dimensional analysis).

Matter can exist in three states—solid, liquid, and gas—and has many levels of organization. Mixtures of compounds can be separated by methods involving only physical changes, such as distillation, filtration, and various forms of chromatography. On the other hand, compounds can be broken down to elements only through chemical changes.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1.
 - a. There are 365 days per year, 24 hours per day, 12 months per year, and 60 minutes per hour. Use these data to determine how many minutes are in a month.
 - b. Now use the following data to calculate the number of minutes in a month: 24 hours per day, 60 minutes per hour, 7 days per week, and 4 weeks per month.
 - c. Why are these answers different? Which (if any) is more correct? Why?
2. You go to a convenience store to buy candy and find the owner to be rather odd. He allows you to buy pieces in multiples of four, and to buy four, you need \$0.23. He only allows you to do this by using 3 pennies and 2 dimes. You have a bunch of pennies and dimes, and instead of counting them, you decide to weigh them. You have 636.3 g of pennies, and each penny weighs 3.03 g. Each dime weighs 2.29 g. Each piece of candy weighs 10.23 g.
 - a. How many pennies do you have?
 - b. How many dimes do you need to buy as much candy as possible?
 - c. How much should all these dimes weigh?
 - d. How many pieces of candy could you buy? (number of dimes from part b)
 - e. How much would this candy weigh?
 - f. How many pieces of candy could you buy with twice as many dimes?
3. When a marble is dropped into a beaker of water, it sinks to the bottom. Which of the following is the best explanation?
 - a. The surface area of the marble is not large enough to be held up by the surface tension of the water.
 - b. The mass of the marble is greater than that of the water.
 - c. The marble weighs more than an equivalent volume of the water.
 - d. The force from dropping the marble breaks the surface tension of the water.
 - e. The marble has greater mass and volume than the water. Justify your choice, and for choices you did not pick, explain what is wrong about them.
4. You have two beakers, one filled to the 100-mL mark with sugar (the sugar has a mass of 180.0 g) and the other filled to the 100-mL mark with water (the water has a mass of 100.0 g). You pour all the sugar and all the water together in a bigger beaker and stir until the sugar is completely dissolved.
 - a. Which of the following is true about the mass of the solution? Explain.
 - i. It is much greater than 280.0 g.
 - ii. It is somewhat greater than 280.0 g.
 - iii. It is exactly 280.0 g.
 - iv. It is somewhat less than 280.0 g.
 - v. It is much less than 280.0 g.
 - b. Which of the following is true about the volume of the solution? Explain.
 - i. It is much greater than 200.0 mL.
 - ii. It is somewhat greater than 200.0 mL.
 - iii. It is exactly 200.0 mL.
 - iv. It is somewhat less than 200.0 mL.
 - v. It is much less than 200.0 mL.
5. You may have noticed that when water boils, you can see bubbles that rise to the surface of the water.
 - a. What is inside these bubbles?
 - i. air
 - ii. hydrogen and oxygen gas
 - iii. oxygen gas
 - iv. water vapor
 - v. carbon dioxide gas
 - b. Is the boiling of water a chemical or physical change? Explain.

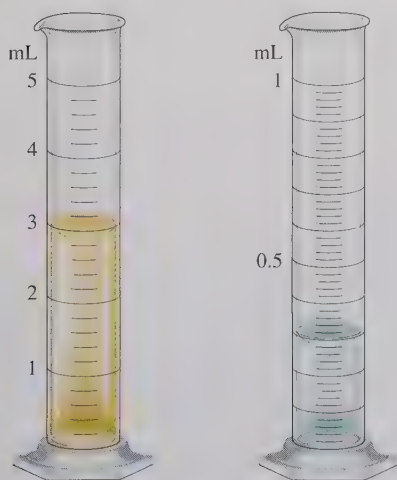
6. If you place a glass rod over a burning candle, the glass appears to turn black. What is happening to each of the following (physical change, chemical change, both, or neither) as the candle burns? Explain each answer.

a. the wax
b. the wick
c. the glass rod

7. Which characteristics of a solid, a liquid, and a gas are exhibited by each of the following substances? How would you classify each substance?

a. a bowl of pudding
b. a bucketful of sand

8. You have water in each graduated cylinder shown:



You then add both samples to a beaker. How would you write the number describing the total volume? What limits the precision of this number?

9. Paracelsus, a sixteenth-century alchemist and healer, adopted as his slogan: "The patients are your textbook, the sickbed is your study." Is this view consistent with using the scientific method?

10. What is wrong with the following statement?

"The results of the experiment do not agree with the theory. Something must be wrong with the experiment."

11. Why is it incorrect to say that the results of a measurement were accurate but not precise?

12. What data would you need to estimate the money you would spend on gasoline to drive your car from New York to Chicago? Provide estimates of values and a sample calculation.

13. Sketch two pieces of glassware: one that can measure volume to the thousandths place and one that can measure volume only to the ones place.

14. You have a 1.0-cm^3 sample of lead and a 1.0-cm^3 sample of glass. You drop each in separate beakers of water. How do the volumes of water displaced by each sample compare? Explain.

15. Sketch a magnified view (showing atoms/molecules) of each of the following and explain:

a. a heterogeneous mixture of two different compounds
b. a homogeneous mixture of an element and a compound

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

16. Define and explain the differences between the following terms.

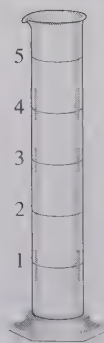
a. law and theory
b. theory and experiment
c. qualitative and quantitative
d. hypothesis and theory

17. Is the scientific method suitable for solving problems only in the sciences? Explain.

18. Which of the following statements (hypotheses) could be tested by quantitative measurement?

a. Ty Cobb was a better hitter than Pete Rose.
b. Ivory soap is $99\frac{44}{100}\%$ pure.
c. Roloids consumes 47 times its weight in excess stomach acid.

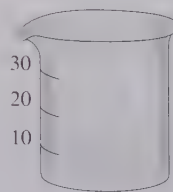
19. For each of the following pieces of glassware, provide a sample measurement and discuss the number of significant figures and uncertainty.



a.



b.



c.

20. A student performed an analysis of a sample for its calcium content and got the following results:

14.92% 14.91% 14.88% 14.91%

The actual amount of calcium in the sample is 15.70%. What conclusion can you draw about the accuracy and precision of these results?

21. Distinguish between physical changes and chemical changes.
22. Why is the separation of mixtures into pure or relatively pure substances so important when performing a chemical analysis?

Exercises

In this section similar exercises are paired.

Significant Figures and Unit Conversions

23. Which of the following are exact numbers?
- The elevation of Breckenridge, Colorado, is 9600 ft.
 - There are 12 eggs in a dozen.
 - One yard is equal to 0.9144 m.
 - The announced attendance at a football game was 52,806.
 - In 1983, 1759 Ph.D.s in chemistry were awarded in the United States.
 - The budget deficit of the U.S. government in fiscal year 1990 was \$269 billion.

24. Which of the following are exact numbers?

- There are 100 cm in 1 m.
- One meter equals 1.094 yard.
- We can use the equation

$$^{\circ}\text{F} = \frac{9}{5}^{\circ}\text{C} + 32$$

to convert from Celsius to Fahrenheit temperature. Are the numbers $\frac{9}{5}$ and 32 exact or inexact?

- $\pi = 3.1415927$.

25. How many significant figures are in each of the following?

- 12
- 1098
- 2001
- 2.001×10^3
- 0.0000101
- 1.01×10^{-5}
- 1000.
- 22.04030

26. How many significant figures are in each of the following?

- 100
- 1.0×10^2
- 1.00×10^3
- 100.
- 0.0048
- 0.00480
- 4.80×10^{-3}
- 4.800×10^{-3}

27. Round off each of the following numbers to three significant figures, and write the answer in standard exponential notation.

- 312.54
- 0.00031254
- 31,254,000
- 0.31254
- 31.254×10^{-3}

28. Use exponential notation to express the number 480 to

- one significant figure
- two significant figures
- three significant figures
- four significant figures

29. Perform the following mathematical operations, and express each result to the correct number of significant figures.

- $97.381 + 4.2502 + 0.99195$
- $171.5 + 72.915 - 8.23$
- $1.00914 + 0.87104 + 1.2012$
- $21.901 - 13.21 - 4.0215$

30. Perform the following mathematical operations, and express each result to the correct number of significant figures.

- $$\frac{0.102 \times 0.0821 \times 273}{1.01}$$
- $0.14 \times 6.022 \times 10^{23}$
- $4.0 \times 10^4 \times 5.021 \times 10^{-3} \times 7.34993 \times 10^2$
- $$\frac{2.00 \times 10^6}{3.00 \times 10^{-7}}$$

31. Perform the following mathematical operations, and express each result to the correct number of significant figures.

- $4.184 \times 100.62 \times (25.27 - 24.16)$
- $$\frac{8.925 - 8.904}{8.925} \times 100$$

(This type of calculation is done many times in calculating a percentage error. Assume that this example is such a calculation; thus 100 can be considered to be an exact number.)

- $(9.04 - 8.23 + 21.954 + 81.0) \div 3.1416$
- $$\frac{9.2 \times 100.65}{8.321 + 4.026}$$
- $0.1654 + 2.07 - 2.114$
- $8.27(4.987 - 4.962)$
- $$\frac{9.5 + 4.1 + 2.8 + 3.175}{4}$$

(Assume that this operation is taking the average of four numbers. Thus 4 in the denominator is exact.)

- $$\frac{9.025 - 9.024}{9.025} \times 100 \text{ (100 is exact)}$$

32. Perform the following mathematical operations, and express the result to the correct number of significant figures.

- $6.022 \times 10^{23} \times 1.05 \times 10^2$
- $$\frac{6.6262 \times 10^{-34} \times 2.998 \times 10^8}{2.54 \times 10^{-9}}$$
- $1.285 \times 10^{-2} + 1.24 \times 10^{-3} + 1.879 \times 10^{-1}$
- $$\frac{1.285 \times 10^{-2} - 1.24 \times 10^{-3}}{(1.00866 - 1.00728)}$$
- 6.02205×10^{23}
- $$\frac{9.875 \times 10^2 - 9.795 \times 10^2}{9.875 \times 10^2} \times 100 \text{ (100 is exact)}$$
- $$\frac{9.42 \times 10^2 + 8.234 \times 10^2 + 1.625 \times 10^3}{3} \text{ (3 is exact)}$$

33. Perform each of the following conversions.

- 8.43 cm to millimeters
- 2.41×10^2 cm to meters
- 294.5 nm to centimeters
- 1.445×10^4 m to kilometers
- 235.3 m to millimeters
- 903.3 nm to micrometers

34. a. How many kilograms are in one teragram?
 b. How many nanometers are in 6.50×10^2 terameters?
 c. How many kilograms are in 25 femtograms?

- d. How many liters are in 8.0 cubic decimeters?
- e. How many microliters are in one milliliter?
- f. How many picograms are in one microgram?

35. Perform the following unit conversions.

- a. Congratulations! You and your spouse are the proud parents of a new baby, born while you are studying in a country that uses the metric system. The nurse has informed you that the baby weighs 3.91 kg and measures 51.4 cm. Convert your baby's weight to pounds and ounces and her length to inches (rounded to the nearest quarter inch).
- b. The circumference of the earth is 25,000 mi at the equator. What is the circumference in kilometers? in meters?
- c. A rectangular solid measures 1.0 m by 5.6 cm by 2.1 dm. Express its volume in cubic meters, liters, cubic inches, and cubic feet.

36. Perform the following unit conversions.

- a. 908 oz to kilograms
- b. 12.8 L to gallons
- c. 125 mL to quarts
- d. 2.89 gal to milliliters
- e. 4.48 lb to grams
- f. 550 mL to quarts

37. Use the following exact conversion factors to perform the stated calculations:

$$5\frac{1}{2} \text{ yards} = 1 \text{ rod}$$

$$40 \text{ rods} = 1 \text{ furlong}$$

$$8 \text{ furlongs} = 1 \text{ mile}$$

- a. The Kentucky Derby race is 1.25 miles. How long is the race in rods, furlongs, meters, and kilometers?
- b. A marathon race is 26 miles, 385 yards. What is this distance in rods, furlongs, meters, and kilometers?

38. Although the preferred SI unit of area is the square meter, land is often measured in the metric system in hectares (ha). One hectare is equal to 10,000 m². In the English system, land is often measured in acres (1 acre = 160 rod²). Use the exact conversions and those given in Exercise 37 to calculate the following.

- a. 1 ha = _____ km².
- b. The area of a 5.5-acre plot of land in hectares, square meters, and square kilometers.
- c. A lot with dimensions 120 ft by 75 ft is to be sold for \$6500. What is the price per acre? What is the price per hectare?

39. Precious metals and gems are measured in troy weights in the English system:

$$24 \text{ grains} = 1 \text{ pennyweight (exact)}$$

$$20 \text{ pennyweight} = 1 \text{ troy ounce (exact)}$$

$$12 \text{ troy ounces} = 1 \text{ troy pound (exact)}$$

$$1 \text{ grain} = 0.0648 \text{ gram}$$

$$1 \text{ carat} = 0.200 \text{ gram}$$

- a. The most common English unit of mass is the pound avoirdupois. What is one troy pound in kilograms and in pounds?
- b. What is the mass of a troy ounce of gold in grams and in carats?
- c. The density of gold is 19.3 g/cm³. What is the volume of a troy pound of gold?

40. Apothecaries (druggists) use the following set of measures in the English system:

$$20 \text{ grains ap} = 1 \text{ scruple (exact)}$$

$$3 \text{ scruples} = 1 \text{ dram ap (exact)}$$

$$8 \text{ dram ap} = 1 \text{ oz ap (exact)}$$

$$1 \text{ dram ap} = 3.888 \text{ g}$$

- a. Is an apothecary grain the same as a troy grain? (See Exercise 39.)
- b. 1 oz ap = _____ oz troy.
- c. An aspirin tablet contains 5.00×10^2 mg of active ingredient. How many grains ap of active ingredient does it contain? How many scruples?
- d. What is the mass of 1 scruple in grams?

41. Science fiction often uses nautical analogies to describe space travel. If the starship *U.S.S. Enterprise* is traveling at warp factor 1.71, what is its speed in knots? (Warp 1.71 = 5.00 times the speed of light; speed of light = 3.00×10^8 m/s; 1 knot = 2000 yd/h, exactly.)

42. The world record for the hundred meter dash is 9.79 s. What is the corresponding average speed in units of m/s, km/h, ft/s, and mi/h? At this speed, how long would it take to run 1.00×10^2 yards?

43. You're planning to buy a new car. One model that you're considering gets 32 miles to a gallon of gasoline in highway travel. The one that your spouse likes gets 14 kilometers to the liter. Which car has the better gas mileage?

44. You pass a road sign saying "New York 112 km." If you drive at a constant speed of 65 mi/h, how long should it take you to reach New York? If your car gets 28 miles to the gallon, how many liters of gasoline are necessary to travel 112 km?

45. You are in Paris and want to buy some peaches for lunch. The sign in the fruit stand indicates that peaches are 4.00 euros per kilogram. Assuming that there are 1.14 euros to the dollar, calculate what a pound of peaches will cost in dollars.

46. A children's pain relief elixir contains 80. mg acetaminophen per 0.50 teaspoon. The dosage recommended for a child who weighs between 24 and 35 lb is 1.5 teaspoons. What is the range of acetaminophen dosages, expressed in mg acetaminophen/kg body weight, for children who weigh between 24 and 35 lb?

Temperature

47. A person has a temperature of 102.5°F. What is this temperature on the Celsius scale? on the Kelvin scale?

48. If the temperature in a room is 74°F , what is this temperature on the Celsius scale? on the Kelvin scale?
49. Convert the following Celsius temperatures to Kelvin and to Fahrenheit degrees.
- the boiling point temperature of ethyl alcohol, 78.1°C
 - a cold wintery day, -25°C
 - the lowest possible temperature, -273°C
 - the melting-point temperature of sodium chloride, 801°C
50. Convert the following Kelvin temperatures to Celsius and Fahrenheit degrees.
- the temperature that registers the same value on both the Fahrenheit and Celsius scales, 233 K
 - the boiling point of helium, 4 K
 - the temperature at which many chemical quantities are determined, 298 K
 - the melting point of tungsten, 3680 K
51. A thermometer gives a reading of $20.6^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. What is the temperature in $^{\circ}\text{F}$? What is the uncertainty?
52. A thermometer gives a reading of $96.1^{\circ}\text{F} \pm 0.2^{\circ}\text{F}$. What is the temperature in $^{\circ}\text{C}$? What is the uncertainty?

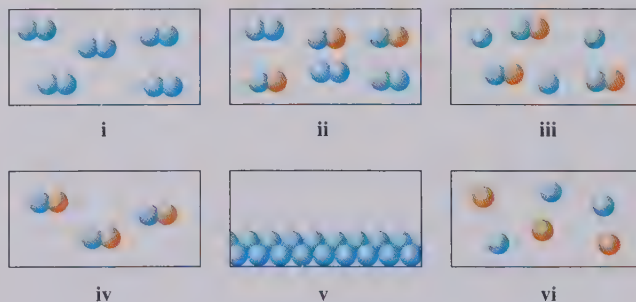
Density

53. The density of aluminum is 2.70 g/cm^3 . Express this value in units of kilograms per cubic meter and pounds per cubic foot.
54. A material will float on the surface of a liquid if the material has a density less than that of the liquid. Given that the density of water is approximately 1.0 g/mL , will a block of material having a volume of $1.2 \times 10^4\text{ in}^3$ and weighing 350 lb float or sink when placed in a reservoir of water?
55. A star is estimated to have a mass of $2 \times 10^{36}\text{ kg}$. Assuming it to be a sphere of average radius $7.0 \times 10^5\text{ km}$, calculate the average density of the star in units of grams per cubic centimeter.
56. A rectangular block has dimensions $2.9\text{ cm} \times 3.5\text{ cm} \times 10.0\text{ cm}$. The mass of the block is 615.0 g . What are the volume and density of the block?
57. Diamonds are measured in carats, and $1\text{ carat} = 0.200\text{ g}$. The density of diamond is 3.51 g/cm^3 . What is the volume of a 5.0-carat diamond?
58. The volume of a diamond is found to be 2.8 mL . What is the mass of the diamond in carats? (See Exercise 57.)
59. A sample containing 33.42 g of metal pellets is poured into a graduated cylinder initially containing 12.7 mL of water, causing the water level in the cylinder to rise to 21.6 mL . Calculate the density of the metal.
60. The density of pure silver is 10.5 g/cm^3 at 20°C . If 5.25 g of pure silver pellets is added to a graduated cylinder containing 11.2 mL of water, to what volume level will the water in the cylinder rise?

61. In each of the following pairs, which has the greater mass? (See Table 1.5.)
- 1.0 kg of feathers or 1.0 kg of lead
 - 1.0 mL of mercury or 1.0 mL of water
 - 19.3 mL of water or 1.00 mL of gold
 - 75 mL of copper or 1.0 L of benzene
62. In each of the following pairs, which has the greater volume?
- 1.0 kg of feathers or 1.0 kg of lead
 - 100 g of gold or 100 g of water
 - 1.0 L of copper or 1.0 L of mercury
63. The density of osmium (the densest metal) is 22.57 g/cm^3 . If a 1.00-kg rectangular block of osmium has two dimensions of $4.00\text{ cm} \times 4.00\text{ cm}$, calculate the third dimension of the block.
64. A copper wire (density = 8.96 g/cm^3) has a diameter of 0.25 mm . If a sample of this copper wire has a mass of 22 g , how long is the wire?

Classification and Separation of Matter

65. What are some of the differences between a solid, a liquid, and a gas?
66. What is the difference between homogeneous and heterogeneous matter? Classify each of the following as homogeneous or heterogeneous.
- soil
 - the atmosphere
 - a carbonated soft drink
 - gasoline
 - gold
 - a solution of ethanol and water
67. Match each description below with the following microscopic pictures. More than one picture may fit each description. A picture may be used more than once or not used at all.



- a gaseous compound
- a mixture of two gaseous elements
- a solid element
- a mixture of a gaseous element and a gaseous compound

68. Classify each of the following as a mixture or a pure substance.

- | | |
|---------------|----------------------|
| a. water | f. uranium |
| b. blood | g. wine |
| c. the oceans | h. leather |
| d. iron | i. table salt (NaCl) |
| e. brass | |

Of the pure substances, which are elements and which are compounds?

69. Classify the following as physical or chemical changes.

- Moth balls gradually vaporize in a closet.
- Hydrofluoric acid attacks glass, and is used to etch calibration marks on glass laboratory utensils.
- A French chef making a sauce with brandy is able to burn off the alcohol from the brandy, leaving just the brandy flavoring.
- Chemistry majors sometimes get holes in the cotton jeans they wear to lab because of acid spills.

70. The properties of a mixture are typically averages of the properties of its components. The properties of a compound may differ dramatically from the properties of the elements that combine to produce the compound. For each process described below, state whether the material being discussed is most likely a mixture or a compound, and state whether the process is a chemical change or a physical change.

- An orange liquid is distilled, resulting in the collection of a yellow liquid and a red solid.
- A colorless, crystalline solid is decomposed, yielding a pale yellow-green gas and a soft, shiny metal.
- A cup of tea becomes sweeter as sugar is added to it.

Additional Exercises

71. A mole of helium gas contains 6.02×10^{23} helium atoms. How many helium atoms are there in a micromole of helium? How many moles of helium does 1.25×10^{20} atoms of helium represent?

72. In Shakespeare's *Richard III*, the First Murderer says:

"Take that, and that! [*Stabs Clarence*]"

If that is not enough, I'll drown you in a malmsey butt within!"

Given that 1 butt = 126 gal, in how many liters of malmsey (a foul brew similar to mead) was the unfortunate Clarence about to be drowned?

73. The contents of one 40. lb bag of topsoil will cover 10. square feet of ground to a depth of 1.0 inch. How many bags are needed to cover a plot which measures 200. by 300. m to a depth of 4.0 cm?

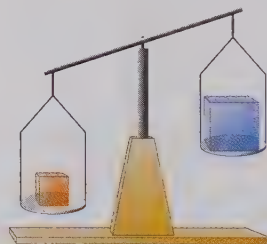
74. In the opening scenes of the movie *Raiders of the Lost Ark*, Indiana Jones tries to remove a gold idol from a booby-trapped pedestal. He replaces the idol with a bag of sand of approximately equal volume. (Density of gold = 19.32 g/cm^3 ; density of sand $\approx 2 \text{ g/cm}^3$.)

- Did he have a reasonable chance of not activating the mass-sensitive booby trap?
- In a later scene he and an unscrupulous guide play catch with the idol. Assume that the volume of the idol is about 1.0 L. If it were solid gold, what mass would the idol have? Is playing catch with it plausible?

75. Mercury poisoning is a debilitating disease that is often fatal. In the human body, mercury reacts with essential enzymes leading to irreversible inactivity of these enzymes. If the amount of mercury in a polluted lake is $0.4 \mu\text{g Hg/mL}$, what is the total mass in kilograms of mercury in the lake? (The lake has a surface area of 100 mi^2 and an average depth of 20 ft.)

76. A 25.00 g-sample of a solid is placed in a graduated cylinder and then the cylinder is filled to the 50.0 mL mark with benzene. The mass of benzene and solid together is 58.80 g. Assuming that the solid is insoluble in benzene and that the density of benzene is 0.880 g/cm^3 , calculate the density of the solid.

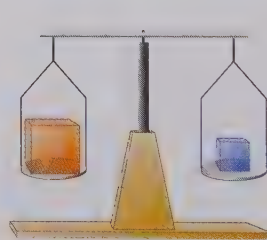
77. For each of the following, decide which block is more dense: the orange block, the blue block, or it cannot be determined. Explain your answers.



a.



b.



c.



d.

78. According to the *Official Rules of Baseball*, a baseball must have a circumference not more than 9.25 in or less than 9.00 in and a mass not more than 5.25 oz or less than 5.00 oz. What range of densities can a baseball be expected to have? Express this range as a single number with an accompanying uncertainty limit.

79. The density of an irregularly shaped object was determined as follows. The mass of the object was found to be $28.90 \text{ g} \pm 0.03 \text{ g}$. A graduated cylinder was partially filled with water. The reading of the level of the water was $6.4 \text{ cm}^3 \pm 0.1 \text{ cm}^3$. The object was dropped in the cylinder, and the level of the water rose to $9.8 \text{ cm}^3 \pm 0.1 \text{ cm}^3$. What is the density of the object with appropriate error limits? (See Appendix 1.5.)

Challenge Problems

80. Many times errors are expressed in terms of percentage. The percent error is the absolute value of the difference of the true value and the experimental value, divided by the true value, and multiplied by 100.

$$\text{Percent error} = \frac{|\text{true value} - \text{experimental value}|}{\text{true value}} \times 100$$

Calculate the percent error for the following measurements.

- The density of an aluminum block determined in an experiment was 2.64 g/cm^3 . (True value 2.70 g/cm^3 .)
 - The experimental determination of iron in iron ore was 16.48%. (True value 16.12%.)
 - A balance measured the mass of a 1.000-g standard as 0.9981 g.
81. A rule of thumb in designing experiments is to avoid using a result that is the small difference between two large measured quantities. In terms of uncertainties in measurement, why is this good advice?
82. A person weighed 15 pennies on a balance and recorded the following masses:

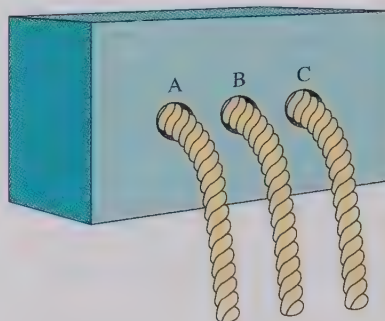
3.112 g	3.109 g	3.059 g
2.467 g	3.079 g	2.518 g
3.129 g	2.545 g	3.050 g
3.053 g	3.054 g	3.072 g
3.081 g	3.131 g	3.064 g

Curious about the results, he looked at the dates on each penny. Two of the light pennies were minted in 1983 and one in 1982. The dates on the 12 heavier pennies ranged from 1970 to 1982. Two of the 12 heavier pennies were minted in 1982.

- Do you think the Bureau of the Mint changed the way it made pennies? Explain.
 - The person calculated the average mass of the 12 heavy pennies. He expressed this average as $3.0828 \text{ g} \pm 0.0482 \text{ g}$. What is wrong with the numbers in this result, and how should the value be expressed?
83. On October 21, 1982, the Bureau of the Mint changed the composition of pennies (see Exercise 82). Instead of an alloy of 95% Cu and 5% Zn by mass, a core of 99.2% Zn and 0.8% Cu with a thin shell of copper was adopted. The overall composition of the new penny was 97.6% Zn and 2.4% Cu by mass. Does this account for the difference in mass among the pennies in Exercise 82? Assume the volume of the individual metals that make up each penny can be added together to give the overall volume of the penny, and assume each penny is the same size. (Density of Cu = 8.96 g/cm^3 ; density of Zn = 7.14 g/cm^3 .)
84. Ethylene glycol is the main component in automobile antifreeze. To monitor the temperature of an auto cooling sys-

tem, you intend to use a meter that reads from 0 to 100. You devise a new temperature scale based on the approximate melting and boiling points of a typical antifreeze solution (-45°C and 115°C). You wish these points to correspond to 0°A and 100°A , respectively.

- Derive an expression for converting between $^\circ\text{A}$ and $^\circ\text{C}$.
 - Derive an expression for converting between $^\circ\text{F}$ and $^\circ\text{A}$.
 - At what temperature would your thermometer and a Celsius thermometer give the same numerical reading?
 - Your thermometer reads 86°A . What is the temperature in $^\circ\text{C}$ and in $^\circ\text{F}$?
 - What is a temperature of 45°C in $^\circ\text{A}$?
85. Confronted with the box shown in the diagram, you wish to discover something about its internal workings. You have no tools and cannot open the box. You pull on rope B, and it moves rather freely. When you pull on rope A, rope C appears to be pulled slightly into the box. When you pull on rope C, rope A almost disappears into the box.*



- Based on these observations, construct a model for the interior mechanism of the box.
 - What further experiments could you do to refine your model?
86. An experiment was performed in which an empty 100-mL graduated cylinder was weighed. It was weighed once again after it had been filled to the 10.0-mL mark with dry sand. A 10-mL pipet was used to transfer 10.00 mL of methanol to the cylinder. The sand-methanol mixture was stirred until bubbles no longer emerged from the mixture and the sand looked uniformly wet. The cylinder was then weighed again. Use the data obtained from this experiment (and displayed at the end of this problem) to find the density of the dry sand, the density of methanol, and the density of sand particles. Does the bubbling that occurs when the methanol is added to the dry sand indicate that the sand and methanol are reacting?

*From Yoder, Suydam, and Snavely, *Chemistry* (New York: Harcourt Brace Jovanovich, 1975), pp. 9–11.

Mass of cylinder plus wet sand	45.2613 g
Mass of cylinder plus dry sand	37.3488 g
Mass of empty cylinder	22.8317 g
Volume of dry sand	10.0 mL
Volume of sand + methanol	17.6 mL
Volume of methanol	10.00 mL

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

87. A cylindrical bar of gold that is 1.5 in high and 0.25 in in diameter has a mass of 23.1984 g, as determined on an analytical balance. An empty graduated cylinder is weighed on a triple-beam balance and has a mass of 73.47 g. After pouring a small amount of a liquid into the graduated cylinder, the mass is 79.16 g. When the gold cylinder is placed in the graduated cylinder (the liquid covers the top of the gold cylinder), the volume indicated on the graduated cylinder is 8.5 mL. Assume that the temperature of the gold bar and the liquid are 86°F. If the density of the liquid decreases by 1.0% for each 10°C rise in temperature (over the range 0 to 50°C), determine
- the density of the gold at 86°F.
 - the density of the liquid at 40°F.

Note: Parts a and b can be answered independently.



Media Activities

- Open Chapter 1 on the student CD. The initial screen for each chapter is a brief overview or summary of the material presented in that chapter of your text. Read the overview to focus your attention on the important topics presented in each chapter.
- Test your understanding of Chapter 1 key terms by opening Key Terms on the CD. For each term, come up with your own definition, and then check your definition by clicking on the specific term. Define the terms out loud with a study partner.
- Test your understanding of Chapter 1 by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

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Atoms, Molecules, and Ions

Where does one start in learning chemistry? Clearly we must consider some essential vocabulary and something about the origins of the science before we can proceed very far. Thus, while Chapter 1 provided background on the fundamental ideas and procedures of science in general, Chapter 2 covers the specific chemical background necessary for understanding the material in the next few chapters. The coverage of these topics is necessarily brief at this point. We will develop these ideas more fully as it becomes appropriate to do so. A major goal of this chapter is to present the systems for naming chemical compounds to provide you with the vocabulary necessary to understand this book and to pursue your laboratory studies.

Because chemistry is concerned first and foremost with chemical changes, we will proceed as quickly as possible to a study of chemical reactions (Chapters 3 and 4). However, before we can discuss reactions, we must consider some fundamental ideas about atoms and how they combine.

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- 2.1 The Early History of Chemistry**
- 2.2 Fundamental Chemical Laws**
- 2.3 Dalton's Atomic Theory**
- 2.4 Early Experiments to Characterize the Atom**
 - The Electron
 - Radioactivity
 - The Nuclear Atom
- 2.5 The Modern View of Atomic Structure: An Introduction**
- 2.6 Molecules and Ions**
- 2.7 An Introduction to the Periodic Table**
- 2.8 Naming Simple Compounds**
 - Binary Ionic Compounds (Type I)
 - Binary Ionic Compounds (Type II)
 - Ionic Compounds with Polyatomic Ions
 - Binary Covalent Compounds (Type III)
 - Formulas from Names
 - Acids

2.1 The Early History of Chemistry

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are just two applications of chemical phenomena that were utilized prior to 1000 B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. they had proposed that all matter was composed of four fundamental substances: fire, earth, water, and air. The Greeks also considered the question of whether matter is continuous, and thus infinitely divisible into smaller pieces, or composed of small, indivisible particles. Supporters of the latter position were Demokritos* of Abdera (c. 460–c. 370 B.C.) and Leucippos, who used the term *atomos* (which later became *atoms*) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas, no definitive conclusion could be reached about the divisibility of matter.

The next 2000 years of chemical history were dominated by a pseudoscience called *alchemy*. Some alchemists were mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, many alchemists were serious scientists, and this period saw important advances: The alchemists discovered several elements and learned to prepare the mineral acids.

The foundations of modern chemistry were laid in the sixteenth century with the development of systematic metallurgy (extraction of metals from ores) by a German, Georg Bauer (1494–1555), and the medicinal application of minerals by a Swiss alchemist/physician known as Paracelsus (full name: Philippus Theophrastus Bombastus von Hohenheim [1493–1541]).

The first “chemist” to perform truly quantitative experiments was Robert Boyle (1627–1691), who carefully measured the relationship between the pressure and volume of air. When Boyle published his book *The Skeptical Chymist* in 1661, the quantitative sciences of physics and chemistry were born. In addition to his results on the quantitative behavior of gases, Boyle’s other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view, a substance was an element unless it could be broken down into two or more simpler substances. As Boyle’s experimental definition of an element became generally accepted, the list of known elements began to grow, and the Greek system of four elements finally died. Although Boyle was an excellent scientist, he was not always right. For example, he clung to the alchemists’ views that metals were not true elements and that a way would eventually be found to change one metal into another.

The phenomenon of combustion evoked intense interest in the seventeenth and eighteenth centuries. The German chemist Georg Stahl (1660–1734) suggested that a substance he called “phlogiston” flowed out of the burning material. Stahl postulated that a substance burning in a closed container eventually stopped burning because the air in the container became saturated with phlogiston. Oxygen gas, discovered by Joseph Priestley (1733–1804),† an English clergyman and scientist (Fig. 2.1), was found to support vigorous combustion and was thus supposed to be low in phlogiston. In fact, oxygen was originally called “dephlogisticated air.”



FIGURE 2.1

The Priestley Medal is the highest honor given by the American Chemical Society. It is named for Joseph Priestley, who was born in England on March 13, 1733. He performed many important scientific experiments, among them the discovery that a gas later identified as carbon dioxide could be dissolved in water to produce *seltzer*. Also, as a result of meeting Benjamin Franklin in London in 1766, Priestley became interested in electricity and is the first to observe that graphite was an electrical conductor. However, his greatest discovery occurred in 1774 when he isolated oxygen by heating mercuric oxide.

Because of his nonconformist political views, Priestley was forced to leave England. He died in the United States in 1804.

*Democritus is an alternate spelling.

†Oxygen gas was actually first observed by the Swedish chemist Karl W. Scheele (1742–1786), but because his results were published after Priestley’s, the latter is commonly credited with the discovery of oxygen.

CHEMICAL IMPACT

There's Gold in Them There Plants!

Gold has always held a strong allure. For example, the alchemists were obsessed with finding a way to transform cheap metals into gold. Also, when gold was discovered in California in 1849, a frantic rush occurred to that area and other areas in the west. Although gold is still valuable, most of the high-grade gold ores have been exhausted. This leaves the low-grade ores—ores with low concentrations of gold that are expensive to process relative to the amount of gold finally obtained.

Now two scientists have come across a novel way to concentrate the gold from low-grade ores. Christopher Anderson and Robert Brooks of Massey University in Palmerston North, New Zealand, have found plants that accumulate gold atoms as they grow in soil containing gold ore [*Nature* 395 (1998): 553]. The plants brassica (of the mustard family) and chicory seem especially effective as botanical “gold miners.” When these plants are dried and burned (after having grown in gold-rich soil), the resulting ash contains approximately 150 ppm (parts per million) of gold. (1 ppm gold represents 1 g of gold in 10^6 g of sample.)

The New Zealand scientists were able to double the amount of gold taken from the soil by the plants by treat-

ing the soil with ammonium thiocyanate (NH_4SCN). The thiocyanate, which reacts with the gold, making it more available to the plants, subsequently breaks down in the soil and therefore poses no environmental hazard.

Thus plants seem to hold great promise as gold miners. They are efficient and reliable and will never go on strike.



This plant from the mustard family is a newly discovered source of gold.

2.2 Fundamental Chemical Laws

By the late eighteenth century, combustion had been studied extensively; the gases carbon dioxide, nitrogen, hydrogen, and oxygen had been discovered; and the list of elements continued to grow. However, it was Antoine Lavoisier (1743–1794), a French chemist (Fig. 2.2), who finally explained the true nature of combustion, thus clearing the way for the tremendous progress that was made near the end of the eighteenth century. Lavoisier, like Boyle, regarded measurement as the essential operation of chemistry. His experiments, in which he carefully weighed the reactants and products of various reactions, suggested that *mass is neither created nor destroyed*. Lavoisier's verification of this **law of conservation of mass** was the basis for the developments in chemistry in the nineteenth century.

Lavoisier's quantitative experiments showed that combustion involved oxygen (which Lavoisier named), not phlogiston. He also discovered that life was supported by a process that also involved oxygen and was similar in many ways to combustion. In 1789 Lavoisier published the first modern chemistry textbook, *Elementary Treatise on Chemistry*, in which he presented a unified picture of the chemical knowledge assembled up to that time. Unfortunately, in the same year the text was published, the French Revolution broke out. Lavoisier, who had been associated with collecting taxes for the government, was executed on the guillotine as an enemy of the people in 1794.

Oxygen is from the French *oxygène*, meaning “generator of acid,” because it was initially considered to be an integral part of all acids.

FIGURE 2.2

Antoine Lavoisier was born in Paris on August 26, 1743. Although Lavoisier's father wanted his son to follow him into the legal profession, young Lavoisier was fascinated by science. From the beginning of his scientific career, Lavoisier recognized the importance of accurate measurements. His careful weighings showed that mass is conserved in chemical reactions and that combustion involves reaction with oxygen. Also, he wrote the first modern chemistry textbook. It is not surprising that Lavoisier is often called the father of modern chemistry.

To help support his scientific work, Lavoisier invested in a private tax-collecting firm and married the daughter of one of the company executives. His connection to the tax collectors proved fatal, for radical French revolutionaries demanded his execution, which occurred on the guillotine on May 8, 1794.



After 1800, chemistry was dominated by scientists who, following Lavoisier's lead, performed careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds. One of these chemists, a Frenchman, Joseph Proust (1754–1826), showed that *a given compound always contains exactly the same proportion of elements by mass*. For example, Proust found that the substance copper carbonate is always 5.3 parts copper to 4 parts oxygen to 1 part carbon (by mass). The principle of the constant composition of compounds, originally called “Proust's law,” is now known as the **law of definite proportion**.

Proust's discovery stimulated John Dalton (1766–1844), an English school-teacher (Fig. 2.3), to think about atoms as the particles that might compose elements. Dalton reasoned that if elements were composed of tiny individual particles, a given compound should always contain the same combination of these atoms. This concept explained why the same relative masses of elements were always found in a given compound.

But Dalton discovered another principle that convinced him even more of the existence of atoms. He noted, for example, that carbon and oxygen form two different compounds that contain different relative amounts of carbon and oxygen, as shown by the following data:

	Mass of Oxygen That Combines with 1 g of Carbon
Compound I	1.33 g
Compound II	2.66 g

Dalton noted that compound II contains twice as much oxygen per gram of carbon as compound I, a fact that could easily be explained in terms of atoms. Compound I

might be CO, and compound II might be CO₂.^{*} This principle, which was found to apply to compounds of other elements as well, became known as the **law of multiple proportions**: *When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.*

To make sure the significance of this observation is clear, in Sample Exercise 2.1 we will consider data for a series of compounds consisting of nitrogen and oxygen.

SAMPLE EXERCISE 2.1

Illustrating the Law of Multiple Proportions

The following data were collected for several compounds of nitrogen and oxygen:

	Mass of Nitrogen That Combines with 1 g of Oxygen
Compound A	1.750 g
Compound B	0.8750 g
Compound C	0.4375 g

Show how these data illustrate the law of multiple proportions.

SOLUTION

For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers. We therefore compute the ratios as follows:

$$\frac{A}{B} = \frac{1.750}{0.875} = \frac{2}{1}$$

$$\frac{B}{C} = \frac{0.875}{0.4375} = \frac{2}{1}$$

$$\frac{A}{C} = \frac{1.750}{0.4375} = \frac{4}{1}$$

These results support the law of multiple proportions.

See Exercises 2.27 and 2.28.



FIGURE 2.3

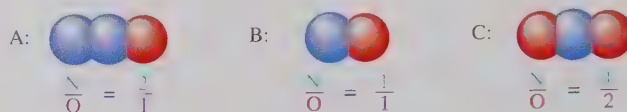
John Dalton (1766–1844), an Englishman, began teaching at a Quaker school when he was 12. His fascination with science included an intense interest in meteorology, which led to an interest in the gases of the air and their ultimate components, atoms. Dalton is best known for his atomic theory, in which he postulated that the fundamental differences among atoms are their masses. He was the first to prepare a table of relative atomic weights.

Dalton was a humble man with several apparent handicaps: He was not articulate and he was color-blind, a terrible problem for a chemist. Despite these disadvantages, he helped to revolutionize the science of chemistry.

The significance of the data in Sample Exercise 2.1 is that compound A contains twice as much nitrogen (N) per gram of oxygen (O) as does compound B and that compound B contains twice as much nitrogen per gram of oxygen as does compound C.

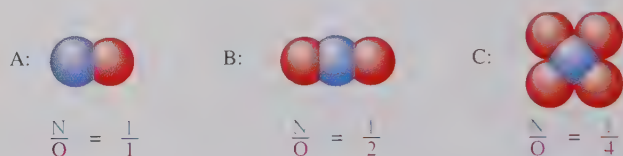
^{*}Subscripts are used to show the numbers of atoms present. The number 1 is understood (not written). The symbols for the elements and the writing of chemical formulas will be illustrated further in Sections 2.6 and 2.7.

These data can be explained readily if the substances are composed of molecules made up of nitrogen atoms and oxygen atoms. For example, one set of possibilities for compounds A, B, and C is



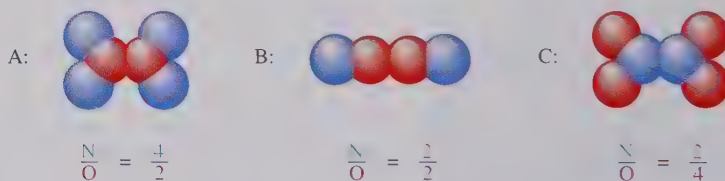
Now we can see that compound A contains 2 atoms of N for every atom of O, whereas compound B contains 1 atom of N per atom of O. That is, compound A contains twice as much nitrogen per given amount of oxygen as does compound B. Similarly, since compound B contains one N per O and compound C contains one N per *two* O's, the nitrogen content of compound C per given amount of oxygen is half that of compound B.

Another set of compounds that fits the data in Sample Exercise 2.1 is



Verify for yourself that these compounds satisfy the requirements.

Still another set that works is



See if you can come up with still another set of compounds that satisfies the data in Sample Exercise 2.1. How many more possibilities are there?

In fact, an infinite number of other possibilities exists. Dalton could not deduce absolute formulas from the available data on relative masses. However, the data on the composition of compounds in terms of the relative masses of the elements supported his hypothesis that each element consisted of a certain type of atom and that compounds were formed from specific combinations of atoms.

2.3 Dalton's Atomic Theory

In 1808 Dalton published *A New System of Chemical Philosophy*, in which he presented his theory of atoms:

1. Each element is made up of tiny particles called atoms.
2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.
3. Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.

These statements are a modern paraphrase of Dalton's ideas.



Joseph Louis Gay-Lussac, a French physicist and chemist, was remarkably versatile. Although he is now known primarily for his studies on the combining of volumes of gases, Gay-Lussac was instrumental in the studies of many of the other properties of gases. Some of Gay-Lussac's motivation to learn about gases arose from his passion for ballooning. In fact, he made ascents to heights of over 4 miles to collect air samples, setting altitude records that stood for about 50 years. Gay-Lussac also was the codiscoverer of boron and the developer of a process for manufacturing sulfuric acid. As chief assayer of the French mint, Gay-Lussac developed many techniques for chemical analysis and invented many types of glassware now used routinely in labs. Gay-Lussac spent his last 20 years as a lawmaker in the French government.

- Chemical reactions involve reorganization of the atoms—changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.

It is instructive to consider Dalton's reasoning on the relative masses of the atoms of the various elements. In Dalton's time water was known to be composed of the elements hydrogen and oxygen, with 8 grams of oxygen present for every 1 gram of hydrogen. If the formula for water were OH, an oxygen atom would have to have 8 times the mass of a hydrogen atom. However, if the formula for water were H_2O (two atoms of hydrogen for every oxygen atom), this would mean that each atom of oxygen is 16 times as massive as *each* atom of hydrogen (since the ratio of the mass of one oxygen to that of *two* hydrogens is 8 to 1). Because the formula for water was not then known, Dalton could not specify the relative masses of oxygen and hydrogen unambiguously. To solve the problem, Dalton made a fundamental assumption: He decided that nature would be as simple as possible. This assumption led him to conclude that the formula for water should be OH. He thus assigned hydrogen a mass of 1 and oxygen a mass of 8.

Using similar reasoning for other compounds, Dalton prepared the first table of **atomic masses** (sometimes called **atomic weights** by chemists, since mass is often determined by comparison to a standard mass—a process called *weighing*). Many of the masses were later proved to be wrong because of Dalton's incorrect assumptions about the formulas of certain compounds, but the construction of a table of masses was an important step forward.

Although not recognized as such for many years, the keys to determining absolute formulas for compounds were provided in the experimental work of the French chemist Joseph Gay-Lussac (1778–1850) and by the hypothesis of an Italian chemist named Amadeo Avogadro (1776–1856). In 1809 Gay-Lussac performed experiments in which he measured (under the same conditions of temperature and pressure) the volumes of gases that reacted with each other. For example, Gay-Lussac found that 2 volumes of hydrogen react with 1 volume of oxygen to form 2 volumes of gaseous water and that 1 volume of hydrogen reacts with 1 volume of chlorine to form 2 volumes of hydrogen chloride. These results are represented schematically in Fig. 2.4.

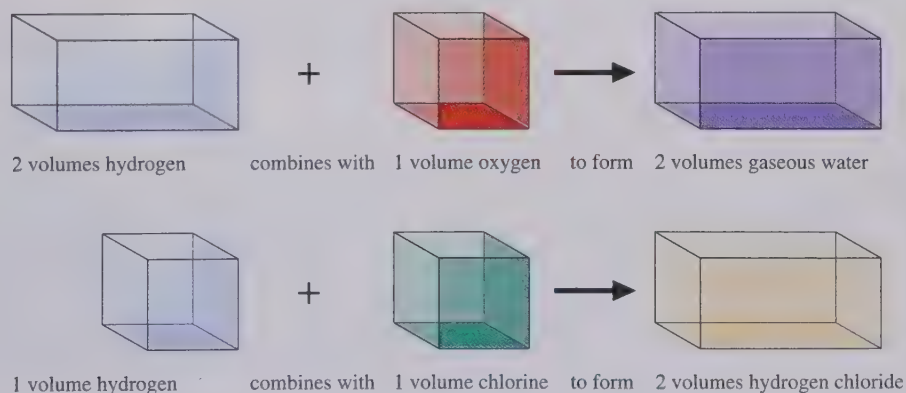


FIGURE 2.4

A representation of some of Gay-Lussac's experimental results on combining gas volumes.

In 1811 Avogadro interpreted these results by proposing that *at the same temperature and pressure, equal volumes of different gases contain the same number of particles*. This assumption (called **Avogadro's hypothesis**) makes sense if the distances between the particles in a gas are very great compared with the sizes of the particles. Under these conditions, the volume of a gas is determined by the number of molecules present, not by the size of the individual particles.

If Avogadro's hypothesis is correct, Gay-Lussac's result,

2 volumes of hydrogen react with 1 volume of oxygen
 $\longrightarrow$ 2 volumes of water vapor

can be expressed as follows:

2 molecules* of hydrogen react with 1 molecule of oxygen
 $\longrightarrow$ 2 molecules of water

These observations can best be explained by assuming that gaseous hydrogen, oxygen, and chlorine are all composed of diatomic (two-atom) molecules: H_2 , O_2 , and Cl_2 , respectively. Gay-Lussac's results can then be represented as shown in Fig. 2.5. (Note that this reasoning suggests that the formula for water is H_2O , not OH as Dalton believed.)

Unfortunately, Avogadro's interpretations were not accepted by most chemists, and a half-century of confusion followed, in which many different assumptions were made about formulas and atomic masses.

During the nineteenth century, painstaking measurements were made of the masses of various elements that combined to form compounds. From these experiments a list of relative atomic masses could be determined. One of the chemists involved in contributing to this list was a Swede named Jöns Jakob Berzelius (1779–1848), who discovered the elements cerium, selenium, silicon, and thorium and developed the modern symbols for the elements used in writing the formulas of compounds.

The Italian chemist Stanislao Cannizzaro (1826–1910) cleared up the confusion in 1860 by doing a series of molar mass determinations that convinced the scientific community that the correct atomic mass of carbon is 12. For more information, see *From Caveman to Chemist* by Hugh Salzberg (American Chemical Society, 1991), p. 223.

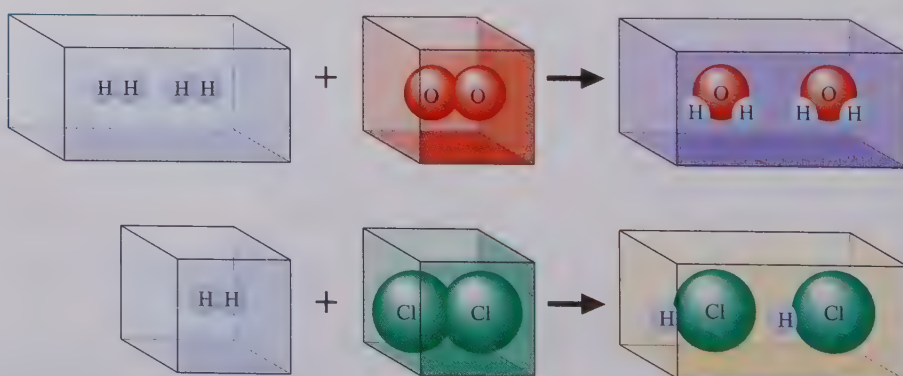


FIGURE 2.5

A representation of combining gases at the molecular level. The spheres represent atoms in the molecules.

*A *molecule* is a collection of atoms (see Section 2.6).

2.4 Early Experiments to Characterize the Atom

On the basis of the work of Dalton, Gay-Lussac, Avogadro, and others, chemistry was beginning to make sense. The concept of atoms was clearly a good idea. Inevitably, scientists began to wonder about the nature of the atom. What is an atom made of, and how do the atoms of the various elements differ?

The Electron

The first important experiments that led to an understanding of the composition of the atom were done by the English physicist J. J. Thomson (Fig. 2.6), who studied electrical discharges in partially evacuated tubes called **cathode-ray tubes** (Fig. 2.7) during the period from 1898 to 1903. Thomson found that when high voltage was applied to the tube, a “ray” he called a *cathode ray* (because it emanated from the negative electrode, or cathode) was produced. Because this ray was produced at the negative electrode and was repelled by the negative pole of an applied electric field (see Fig. 2.8), Thomson postulated that the ray was a stream of negatively charged particles, now called **electrons**. From experiments in which he measured the deflection of the beam of electrons in a magnetic field, Thomson determined the *charge-to-mass ratio* of an electron:

$$\frac{e}{m} = -1.76 \times 10^8 \text{ C/g}$$

where e represents the charge on the electron in coulombs (C) and m represents the electron mass in grams.

One of Thomson’s primary goals in his cathode-ray tube experiments was to gain an understanding of the structure of the atom. He reasoned that since electrons could be produced from electrodes made of various types of metals, *all* atoms must contain electrons. Since atoms were known to be electrically neutral, Thomson further assumed that atoms also must contain some positive charge. Thomson postulated that an atom consisted of a diffuse cloud of positive charge with the negative electrons embedded randomly in it. This model, shown in Fig. 2.9, is often called



FIGURE 2.6

J. J. Thomson (1856–1940) was an English physicist at Cambridge University. He received the Nobel Prize in physics in 1906.

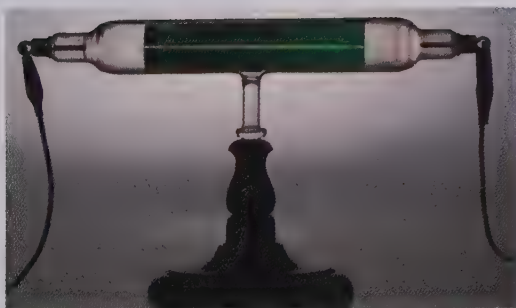
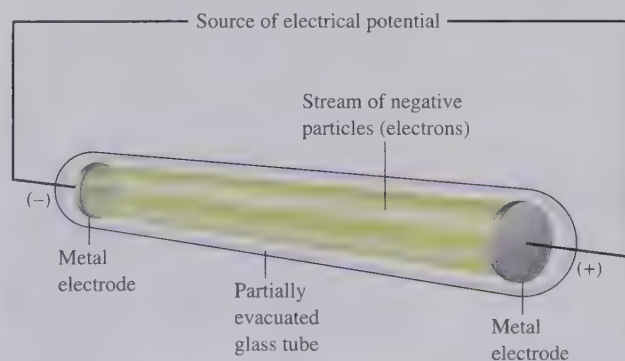


FIGURE 2.7

A cathode-ray tube. The fast-moving electrons excite the gas in the tube, causing a glow between the electrodes. The green color in the photo is due to the response of the screen (coated with zinc sulfide) to the electron beam.



Berzelius, Selenium, and Silicon

Jons Jakob Berzelius was probably the best experimental chemist of his generation and, given the crudeness of his laboratory equipment, maybe the best of all time. Unlike Lavoisier, who could afford to buy the best laboratory equipment available, Berzelius worked with minimal equip-

Comparison of Several of Berzelius's Atomic Masses with the Modern Values

Element	Atomic Mass	
	Berzelius's Value	Current Value
Chlorine	35.41	35.45
Copper	63.00	63.55
Hydrogen	1.00	1.01
Lead	207.12	207.2
Nitrogen	14.05	14.01
Oxygen	16.00	16.00
Potassium	39.19	39.10
Silver	108.12	107.87
Sulfur	32.18	32.07

ment in very plain surroundings. One of Berzelius's students described the Swedish chemist's workplace: "The laboratory consisted of two ordinary rooms with the very simplest arrangements; there were neither furnaces nor hoods, neither water system nor gas. Against the walls stood some closets with the chemicals, in the

middle the mercury trough and the blast lamp table. Beside this was the sink consisting of a stone water holder with a stopcock and a pot standing under it. [Next door in the kitchen] stood a small heating furnace."

In these simple facilities Berzelius performed more than 2000 experiments over a 10-year period to determine accurate atomic masses for the 50 elements then known. His success can be seen from the data in the table at left. These remarkably accurate values attest to his experimental skills and patience.

Besides his table of atomic masses, Berzelius made many other major contributions to chemistry. The most important of these was the invention of a simple set of symbols for the elements along with a system for writing the formulas of compounds to replace the awkward symbolic representations of the alchemists. Although some chemists, including Dalton, objected to the new system, it was gradually adopted and forms the basis of the system we use today.

In addition to these accomplishments, Berzelius also discovered the elements cerium, thorium, selenium, and silicon. Of these elements, selenium and silicon are particularly important in today's world. Berzelius discovered

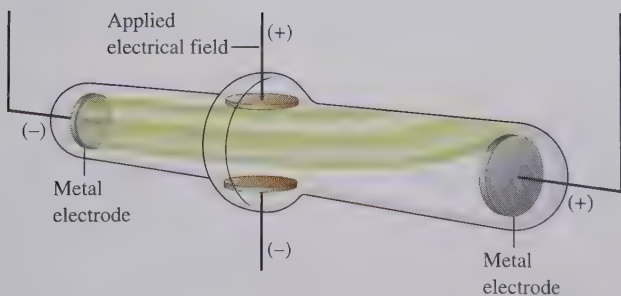


FIGURE 2.8
Deflection of cathode rays by an applied electric field.

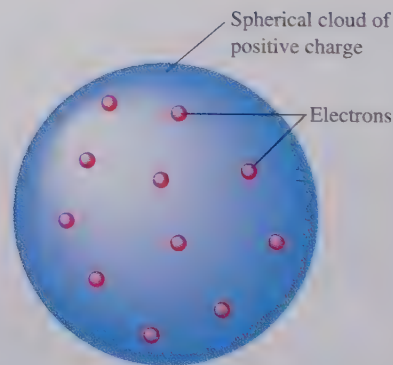


FIGURE 2.9
The plum pudding model of the atom.

the *plum pudding model* because the electrons are like raisins dispersed in a pudding (the positive charge cloud), as in plum pudding, a favorite English dessert.*

In 1909 Robert Millikan (1868–1953), working at the University of Chicago, performed very clever experiments involving charged oil drops. These experiments

*Although J. J. Thomson is generally given credit for this model, the idea was apparently first suggested by the English mathematician and physicist William Thomson (better known as Lord Kelvin and not related to J. J. Thomson).

The Alchemists' Symbols for Some Common Elements and Compounds

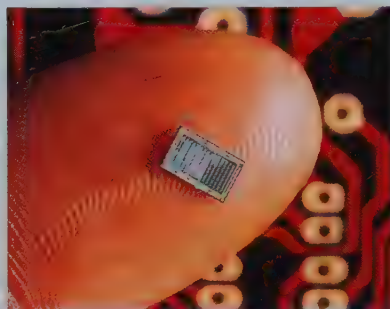
Substance	Alchemists' Symbol
Silver	
Lead	
Tin	
Platinum	
Sulfuric acid	
Alcohol	
Sea salt	

selenium in 1817 in connection with his studies of sulfuric acid. For years selenium's toxicity has been known, but only recently have we become aware that it may have a positive effect on human health. Studies have shown that trace amounts of selenium in the diet may protect people from heart disease and cancer. One study based on data from 27 countries showed an inverse

relationship between the cancer death rate and the selenium content of soil in a particular region (low cancer death rate in areas with high selenium content). Another research paper reported an inverse relationship between the selenium content of the blood and the incidence of breast cancer in women. A study reported in 1998 used the toenail clippings of 33,737 men to show that selenium seems to protect against prostate cancer. Selenium is also found in

the heart muscle and may play an important role in proper heart function. Because of these and other studies, selenium's reputation has improved, and many scientists are now studying its function in the human body.

Silicon is the second most abundant element in the earth's crust, exceeded only by oxygen. As we will see in Chapter 10, compounds involving silicon bonded to oxygen make up most of the earth's sand, rock, and soil. Berzelius prepared silicon in its pure form in 1824 by heating silicon tetrafluoride (SiF_4) with potassium metal. Today, silicon forms the basis for the modern microelectronics industry centered near San Francisco in a place that has come to be known as "Silicon Valley." The technology of the silicon



A silicon chip.

chip (see figure) with its printed circuits has transformed computers from room-sized monsters with thousands of unreliable vacuum tubes to desktop and notebook-sized units with trouble-free "solid-state" circuitry.

See E. J. Holmyard, *Alchemy* (New York: Penguin Books, 1968).

allowed him to determine the magnitude of the electron charge (see Fig. 2.10). With this value and the charge-to-mass ratio determined by Thomson, Millikan was able to calculate the mass of the electron as 9.11×10^{-31} kilogram.

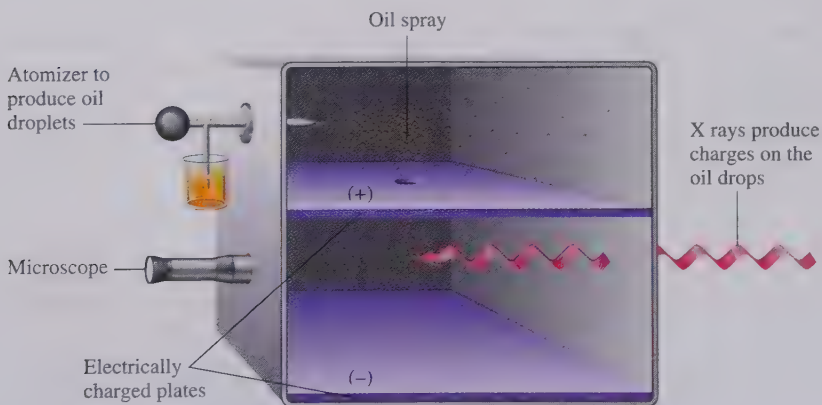


FIGURE 2.10

A schematic representation of the apparatus Millikan used to determine the charge on the electron. The fall of charged oil droplets due to gravity can be halted by adjusting the voltage across the two plates. This voltage and the mass of the oil drop can then be used to calculate the charge on the oil drop. Millikan's experiments showed that the charge on an oil drop is always a whole-number multiple of the electron charge.



A technician using a scanner to monitor the uptake of radioactive iodine in a patient's thyroid.

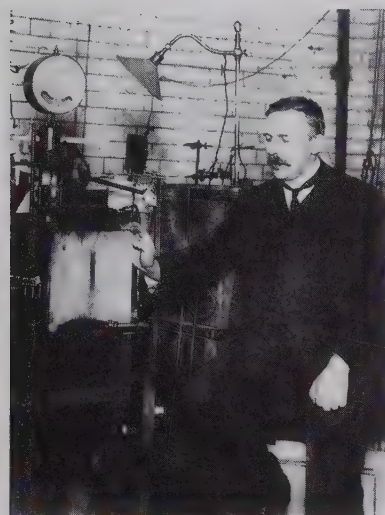


FIGURE 2.11

Ernest Rutherford (1871–1937) was born on a farm in New Zealand. In 1895 he placed second in a scholarship competition to attend Cambridge University but was awarded the scholarship when the winner decided to stay home and get married. As a scientist in England, Rutherford did much of the early work on characterizing radioactivity. He named the α and β particles and the γ ray and coined the term *half-life* to describe an important attribute of radioactive elements. His experiments on the behavior of α particles striking thin metal foils led him to postulate the nuclear atom. He also invented the name *proton* for the nucleus of the hydrogen atom. He received the Nobel Prize in chemistry in 1908.

Radioactivity

In the late nineteenth century scientists discovered that certain elements produce high-energy radiation. For example, in 1896 the French scientist Henri Becquerel found accidentally that a piece of a mineral containing uranium could produce its image on a photographic plate in the absence of light. He attributed this phenomenon to a spontaneous emission of radiation by the uranium, which he called **radioactivity**. Studies in the early twentieth century demonstrated three types of radioactive emission: gamma (γ) rays, beta (β) particles, and alpha (α) particles. A γ ray is high-energy “light”; a β particle is a high-speed electron; and an α particle has a $2+$ charge, that is, a charge twice that of the electron and with the opposite sign. The mass of an α particle is 7300 times that of the electron. More modes of radioactivity are now known, and we will discuss them in Chapter 18. Here we will consider only α particles because they were used in some crucial early experiments.

The Nuclear Atom

In 1911 Ernest Rutherford (Fig. 2.11), who performed many of the pioneering experiments to explore radioactivity, carried out an experiment to test Thomson’s plum pudding model. The experiment involved directing α particles at a thin sheet of metal foil, as illustrated in Fig. 2.12. Rutherford reasoned that if Thomson’s model were accurate, the massive α particles should crash through the thin foil like cannonballs through gauze, as shown in Fig. 2.13(a). He expected the α particles to travel through the foil with, at the most, very minor deflections in their paths. The results of the experiment were very different from those Rutherford anticipated. Although most of the α particles passed straight through, many of the particles were deflected at large angles, as shown in Fig. 2.13(b), and some were reflected, never hitting the detector. This outcome was a great surprise to Rutherford. (He wrote that this result was comparable with shooting a howitzer at a piece of paper and having the shell reflected back.)

Rutherford knew from these results that the plum pudding model for the atom could not be correct. The large deflections of the α particles could be caused only by a center of concentrated positive charge that contains most of the atom’s mass, as illustrated in Fig. 2.13(b). Most of the α particles pass directly through the foil because the atom is mostly open space. The deflected α particles are those that had

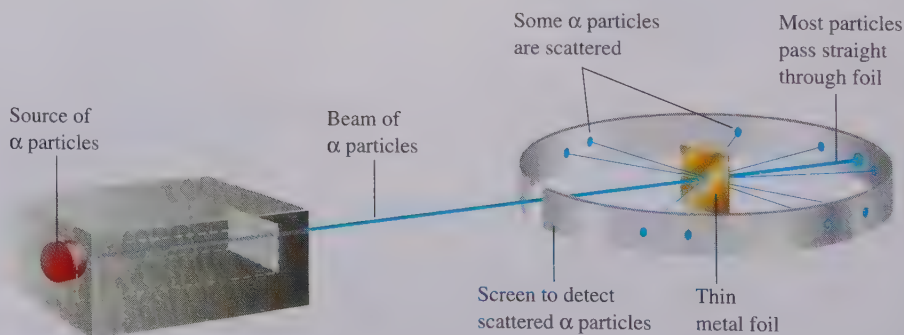


FIGURE 2.12

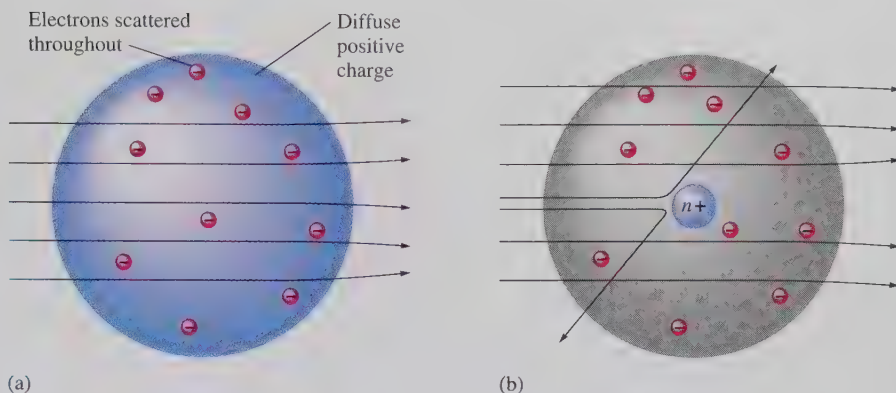
Rutherford’s experiment on α -particle bombardment of metal foil.



Visualization: Scattering of Alpha Particles by Gold Foil

FIGURE 2.13

(a) The expected results of the metal foil experiment if Thomson's model were correct. (b) Actual results.



a “close encounter” with the massive positive center of the atom, and the few reflected α particles are those that made a “direct hit” on the much more massive positive center.

In Rutherford's mind these results could be explained only in terms of a **nuclear atom**—an atom with a dense center of positive charge (the **nucleus**) with electrons moving around the nucleus at a distance that is large relative to the nuclear radius.

2.5

The Modern View of Atomic Structure: An Introduction

The forces that bind the positively charged protons in the nucleus will be discussed in Chapter 18.

In the years since Thomson and Rutherford, a great deal has been learned about atomic structure. Because much of this material will be covered in detail in later chapters, only an introduction will be given here. The simplest view of the atom is that it consists of a tiny nucleus (with a diameter of about 10^{-13} cm) and electrons that move about the nucleus at an average distance of about 10^{-8} cm from it (see Fig. 2.14).

As we will see later, the chemistry of an atom mainly results from its electrons. For this reason, chemists can be satisfied with a relatively crude nuclear model. The nucleus is assumed to contain **protons**, which have a positive charge equal in magnitude to the electron's negative charge, and **neutrons**, which have virtually the same mass as a proton but no charge. The masses and charges of the electron, proton, and neutron are shown in Table 2.1.

TABLE 2.1 The Mass and Charge of the Electron, Proton, and Neutron

Particle	Mass	Charge*
Electron	9.11×10^{-31} kg	$1-$
Proton	1.67×10^{-27} kg	$1+$
Neutron	1.67×10^{-27} kg	None

*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

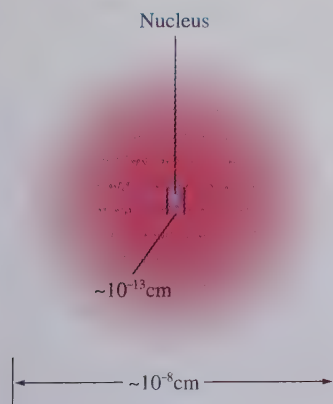
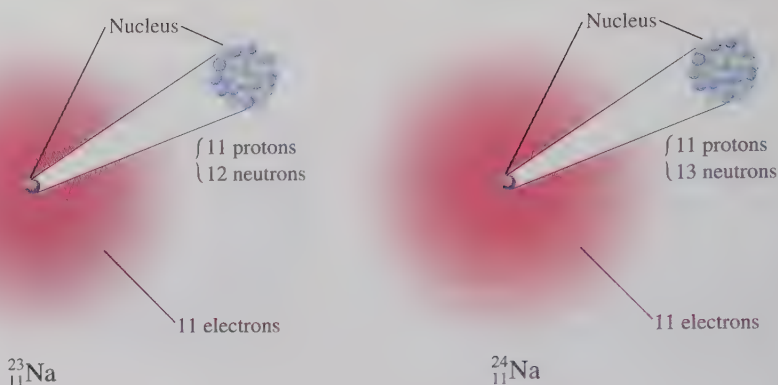


FIGURE 2.14

A nuclear atom viewed in cross section. Note that this drawing is not to scale.

**FIGURE 2.15**

Two isotopes of sodium. Both have eleven protons and eleven electrons, but they differ in the number of neutrons in their nuclei.

The *chemistry* of an atom arises from its electrons.



If the atomic nucleus were the size of this ball bearing, a typical atom would be the size of this stadium.

Mass number $\rightarrow$ ^{4}X $\leftarrow$ Element symbol
Atomic number $\rightarrow$ $^{4}_{2}\text{X}$ $\leftarrow$ Element symbol

Mass number $\rightarrow$ $^{23}_{11}\text{Na}$ $\leftarrow$ Element symbol
Atomic number $\rightarrow$ $^{23}_{11}\text{Na}$ $\leftarrow$ Element symbol

Two striking things about the nucleus are its small size compared with the overall size of the atom and its extremely high density. The tiny nucleus accounts for almost all the atom's mass. Its great density is dramatically demonstrated by the fact that a piece of nuclear material about the size of a pea would have a mass of 250 million tons!

An important question to consider at this point is, "If all atoms are composed of these same components, why do different atoms have different chemical properties?" The answer to this question lies in the number and the arrangement of the electrons. The electrons constitute most of the atomic volume and thus are the parts that "intermingle" when atoms combine to form molecules. Therefore, the number of electrons possessed by a given atom greatly affects its ability to interact with other atoms. As a result, the atoms of different elements, which have different numbers of protons and electrons, show different chemical behavior.

A sodium atom has 11 protons in its nucleus. Since atoms have no net charge, the number of electrons must equal the number of protons. Therefore, a sodium atom has 11 electrons moving around its nucleus. It is *always* true that a sodium atom has 11 protons and 11 electrons. However, each sodium atom also has neutrons in its nucleus, and different types of sodium atoms exist that have different numbers of neutrons. For example, consider the sodium atoms represented in Fig. 2.15. These two atoms are **isotopes**, or *atoms with the same number of protons but different numbers of neutrons*. Note that the symbol for one particular type of sodium atom is written

where the **atomic number** Z (number of protons) is written as a subscript, and the **mass number** A (the total number of protons and neutrons) is written as a superscript. (The particular atom represented here is called "sodium twenty-three." It has 11 electrons, 11 protons, and 12 neutrons.) Because the chemistry of an atom is due to its electrons, isotopes show almost identical chemical properties. In nature most elements contain mixtures of isotopes.

SAMPLE EXERCISE 2.2

Writing the Symbols for Atoms

Write the symbol for the atom that has an atomic number of 9 and a mass number of 19. How many electrons and how many neutrons does this atom have?

Reading the History of Bogs

Scientists often “read” the history of the earth and its inhabitants using very different “books” than traditional historians. For example, the disappearance of the dinosaurs 65 million years ago in an “instant” of geological time was a great mystery until unusually high iridium and osmium levels were discovered at a position in the earth’s crust corresponding to that time. These high levels of iridium and osmium suggested that an extraterrestrial object had struck the earth 65 million years ago with catastrophic results for the dinosaurs. Since then, the huge buried crater caused by the object has been discovered on the Yucatan Peninsula, and virtually everyone is now convinced that this is the correct explanation for the disappearing dinosaurs.

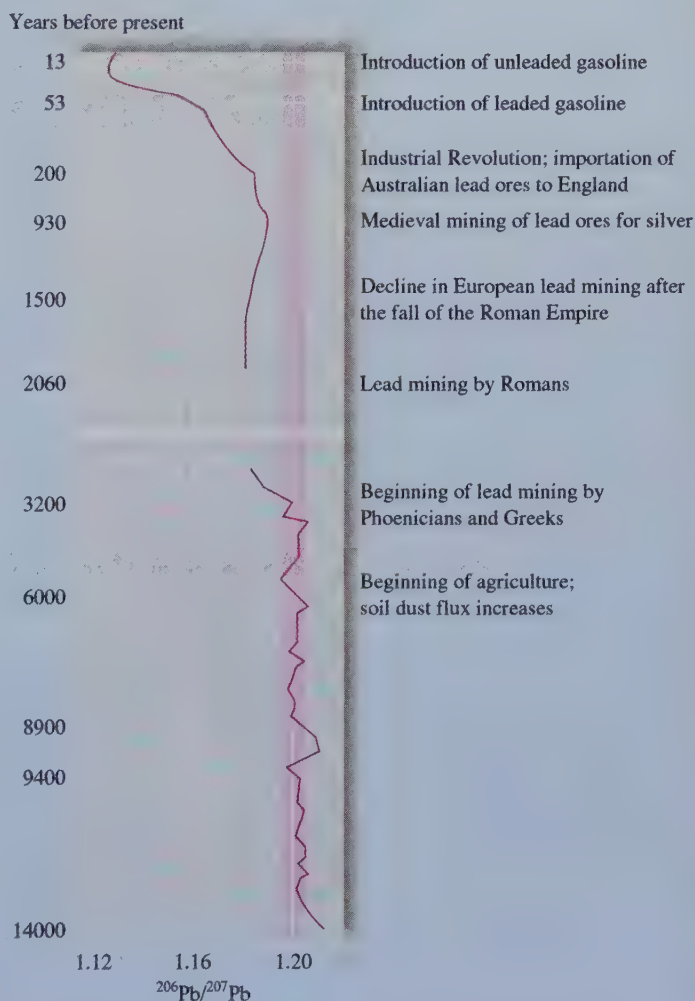
History is also being “read” by scientists studying ice cores from glaciers in Iceland. Now Swiss scientists have found that ancient peat bogs can furnish a reliable historical record. Geochemist William Shotyk of the University of Bern has found a 15,000-year window on history by analyzing the lead content of core samples from a Swiss mountainside peat bog [*Science* 281 (1998): 1635]. Various parts of the core samples were dated by ^{14}C dating techniques (see Chapter 18, Section 18.4, for more information) and analyzed for their scandium and lead contents. Also, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was measured for each sample. These data are represented in the accompanying figure. Notice that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio remains very close to 1.20 (see the red band in the figure) from 14,000 years to 3200 years. The value of 1.20 is the same as the average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the earth’s soil.

The core also reveals that the total lead and scandium levels increased simultaneously at the 6000-year mark but that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio remained close to 1.20. This coincides with the beginning of agriculture in Europe, which caused more soil dust to enter the atmosphere.

Significantly, about 3000 years ago the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreased markedly. This also corresponds in the core sample to an increase in total lead content out of proportion to the increase in scandium. This indicates the lead no longer resulted from soil dust but from other activities of humans—lead mining had begun. Since the 3000-year mark, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has remained well below 1.20, indi-

cating that human use of lead ores has become the dominant source of airborne lead. This is confirmed by the sharp decline in the ratio beginning 200 years ago that corresponds to the importation into England of Australian lead ores having low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios.

So far only lead has been used to read the history in the bog. However, Shotyk’s group is also measuring the changes in the levels of copper, zinc, cadmium, arsenic, mercury, and antimony. More interesting stories are sure to follow.



Geochemist William Shotyk’s analysis of the lead content of ice core samples reveals a 15,000-year history of lead levels. (Note: Dates are based on calibrated radiocarbon dating. Because the core was retrieved in two segments, a break in data occurs between 2060 and 3200 years before present.)

SOLUTION

The atomic number 9 means the atom has 9 protons. This element is called *fluorine*, symbolized by F. The atom is represented as



and is called “fluorine nineteen.” Since the atom has 9 protons, it also must have 9 electrons to achieve electrical neutrality. The mass number gives the total number of protons and neutrons, which means that this atom has 10 neutrons.

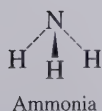
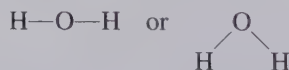
See Exercises 2.43 through 2.46.

2.6 Molecules and Ions

From a chemist’s viewpoint, the most interesting characteristic of an atom is its ability to combine with other atoms to form compounds. It was John Dalton who first recognized that chemical compounds are collections of atoms, but he could not determine the structure of atoms or their means for binding to each other. During the twentieth century we learned that atoms have electrons and that these electrons participate in bonding one atom to another. We will discuss bonding thoroughly in Chapters 8 and 9; here we will introduce some simple bonding ideas that will be useful in the next few chapters.

The forces that hold atoms together in compounds are called **chemical bonds**. One way that atoms can form bonds is by *sharing electrons*. These bonds are called **covalent bonds**, and the resulting collection of atoms is called a **molecule**. Molecules can be represented in several different ways. The simplest method is the **chemical formula**, in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to indicate the relative numbers of atoms. For example, the formula for carbon dioxide is CO_2 , meaning that each molecule contains 1 atom of carbon and 2 atoms of oxygen.

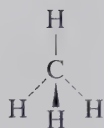
Examples of molecules that contain covalent bonds are hydrogen (H_2), water (H_2O), oxygen (O_2), ammonia (NH_3), and methane (CH_4). More information about a molecule is given by its **structural formula**, in which the individual bonds are shown (indicated by lines). Structural formulas may or may not indicate the actual shape of the molecule. For example, water might be represented as



The structure on the right shows the actual shape of the water molecule. Scientists know from experimental evidence that the molecule looks like this. (We will study the shapes of molecules further in Chapter 8.) The structural formula for ammonia is shown in the margin at left.

Note that atoms connected to the central atom by dashed lines are behind the plane of the paper, and atoms connected to the central atom by wedges are in front of the plane of the paper.

In a compound composed of molecules, the individual molecules move around as independent units. For example, a molecule of methane gas can be represented in several ways. The structural formula for methane (CH_4) is shown in Fig. 2.16. The **space-filling model** of methane, which shows the relative sizes of the atoms as well as their relative orientation in the molecule, is given in Fig. 2.17. **Ball-and-**



Methane

FIGURE 2.16

The structural formula for methane.

**FIGURE 2.17**

Space-filling model of methane. This type of model shows both the relative sizes of the atoms in the molecule and their spatial relationships.

**FIGURE 2.18**

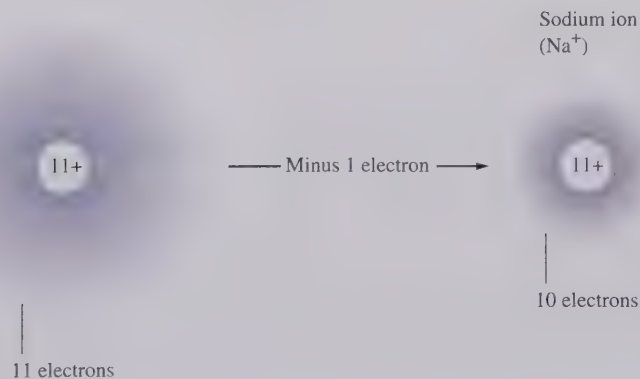
Ball-and-stick model of methane.

stick models are also used to represent molecules. The ball-and-stick structure of methane is shown in Fig. 2.18.

A second type of chemical bond results from attractions among ions. An **ion** is an atom or group of atoms that has a net positive or negative charge. The best-known ionic compound is common table salt, or sodium chloride, which forms when neutral chlorine and sodium react.

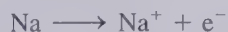
To see how the ions are formed, consider what happens when an electron is transferred from a sodium atom to a chlorine atom (the neutrons in the nuclei will be ignored):

Neutral sodium
atom (Na)

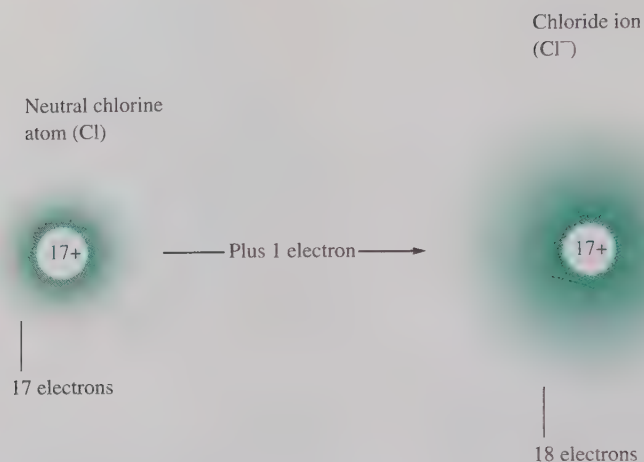


Na^+ is usually called the *sodium ion* rather than the sodium cation. Also Cl^- is called the *chloride ion* rather than the chloride anion. In general, when a specific ion is referred to, the word *ion* rather than cation or anion is used.

With one electron stripped off, the sodium, with its 11 protons and only 10 electrons, now has a net 1+ charge—it has become a *positive ion*. A positive ion is called a **cation**. The sodium ion is written as Na^+ , and the process can be represented in shorthand form as



If an electron is added to chlorine,



the 18 electrons produce a net $1-$ charge; the chlorine has become an *ion with a negative charge*—an **anion**. The chloride ion is written as Cl^- , and the process is represented as



Because anions and cations have opposite charges, they attract each other. This *force of attraction between oppositely charged ions* is called **ionic bonding**. As illustrated in Fig. 2.19, sodium metal and chlorine gas (a green gas composed of Cl_2 molecules) react to form solid sodium chloride, which contains many Na^+ and Cl^- ions packed together and forms the beautiful colorless cubic crystals shown in Fig. 2.19.

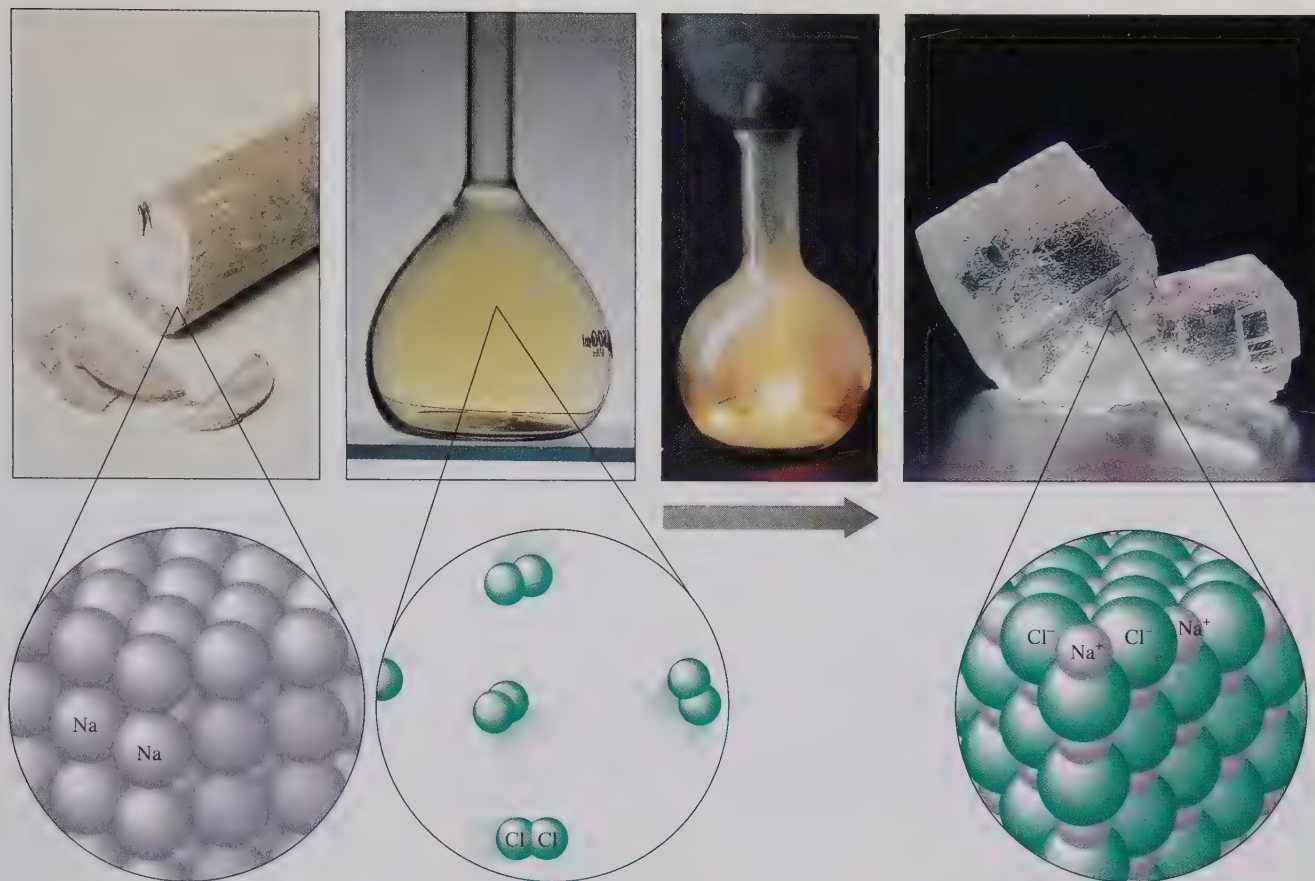
A solid consisting of oppositely charged ions is called an **ionic solid**, or a **salt**. Ionic solids can consist of simple ions, as in sodium chloride, or of **polyatomic** (many atom) **ions**, as in ammonium nitrate (NH_4NO_3), which contains ammonium ions (NH_4^+) and nitrate ions (NO_3^-). The ball-and-stick models of these ions are shown in Fig. 2.20.

2.7 An Introduction to the Periodic Table

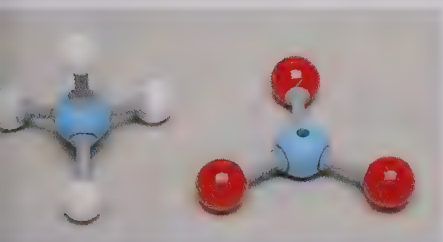
In a room where chemistry is taught or practiced, a chart called the **periodic table** is almost certain to be found hanging on the wall. This chart shows all the known elements and gives a good deal of information about each. As our study of chemistry progresses, the usefulness of the periodic table will become more obvious. This section will simply introduce it to you.

A simplified version of the periodic table is shown in Fig. 2.21. The letters in the boxes are the symbols for the elements; these abbreviations are based on the current element names or the original names* (see Table 2.2). The number shown

*See David W. Ball, "Elemental Etymology: What's in a Name?" *J. Chem. Ed.* **62** (1985): 787.

**FIGURE 2.19**

Sodium metal (which is so soft it can be cut with a knife and which consists of individual sodium atoms) reacts with chlorine gas (which contains Cl_2 molecules) to form solid sodium chloride (which contains Na^+ and Cl^- ions packed together).

**FIGURE 2.20**

Ball-and-stick models of the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-).

Metals tend to form positive ions; nonmetals tend to form negative ions.

above each symbol is the *atomic number* (number of protons) for that element. For example, carbon (C) has atomic number 6, and lead (Pb) has atomic number 82. Most of the elements are **metals**. Metals have characteristic physical properties such as efficient conduction of heat and electricity, malleability (they can be hammered into thin sheets), ductility (they can be pulled into wires), and (often) a lustrous appearance. Chemically, metals tend to *lose* electrons to form positive ions. For example, copper is a typical metal. It is lustrous (although it tarnishes readily); it is an excellent conductor of electricity (it is widely used in electrical wires); and it is readily formed into various shapes, such as pipes for water systems. Copper is also found in many salts, such as the beautiful blue copper sulfate, in which copper is present as Cu^{2+} ions. Copper is a member of the transition metals—the metals shown in the center of the periodic table.

The relatively few **nonmetals** appear in the upper-right corner of the table (to the right of the heavy line in Fig. 2.21), except hydrogen, a nonmetal that resides in the upper-left corner. The nonmetals lack the physical properties that characterize the metals. Chemically, they tend to *gain* electrons in reactions with metals to

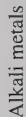
**FIGURE 2.21**

TABLE 2.2 The Symbols for the Elements That Are Based on the Original Names

Current Name	Original Name	Symbol
Antimony	Stibium	Sb
Copper	Cuprum	Cu
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mercury	Hydrargyrum	Hg
Potassium	Kalium	K
Silver	Argentum	Ag
Sodium	Natrium	Na
Tin	Stannum	Sn
Tungsten	Wolfram	W

CHEMICAL IMPACT

Hassium Fits Right in

Hassium, element 108, does not exist in nature but must be made in a particle accelerator. It was first created in 1984 and can be made by shooting magnesium-26 ($^{26}_{12}\text{Mg}$) atoms at curium-248 ($^{248}_{96}\text{Cm}$) atoms. The collisions between these atoms produce some hassium-265 ($^{265}_{108}\text{Hs}$) atoms. The position of hassium in the periodic table (see Fig. 2.21) in the vertical column containing iron, ruthenium, and osmium suggests that hassium should have chemical properties similar to these metals. However, it is not easy to test this prediction—only a few atoms of hassium can be made at a given time and they last for only about 9 seconds. Imagine having to get your next lab experiment done in 9 seconds!

Amazingly, a team of chemists from the Lawrence Berkeley National Laboratory in California, the Paul Scher-

rer Institute and the University of Bern in Switzerland, and the Institute of Nuclear Chemistry in Germany have done experiments to characterize the chemical behavior of hassium. For example, they have observed that hassium atoms react with oxygen to form a hassium oxide compound of the type expected from its position on the periodic table. The team has also measured other properties of hassium, including the energy released as it undergoes nuclear decay to another atom.

This work would have surely pleased Dmitri Mendeleev (see Fig. 7.23), who originally developed the periodic table and showed its power to predict chemical properties.

Elements in the same vertical column in the periodic table form a **group** (or **family**) and generally have similar properties.



Samples of chlorine gas, liquid bromine, and solid iodine.

Another format of the periodic table will be discussed in Section 7.11.

form negative ions. Nonmetals often bond to each other by forming covalent bonds. For example, chlorine is a typical nonmetal. Under normal conditions it exists as Cl_2 molecules; it reacts with metals to form salts containing Cl^- ions (NaCl , for example); and it forms covalent bonds with nonmetals (for example, hydrogen chloride gas, HCl).

The periodic table is arranged so that elements in the same vertical columns (called **groups** or **families**) have *similar chemical properties*. For example, all of the **alkali metals**, members of Group 1A—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)—are very active elements that readily form ions with a 1+ charge when they react with nonmetals. The members of Group 2A—beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)—are called the **alkaline earth metals**. They all form ions with a 2+ charge when they react with nonmetals. The **halogens**, the members of Group 7A—fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At)—all form diatomic molecules. Fluorine, chlorine, bromine, and iodine all react with metals to form salts containing ions with a 1− charge (F^- , Cl^- , Br^- , and I^-). The members of Group 8A—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)—are known as the **noble gases**. They all exist under normal conditions as monatomic (single-atom) gases and have little chemical reactivity.

Note from Fig. 2.21 that alternate sets of symbols are used to denote the groups. The symbols 1A through 8A are the traditional designations, whereas the numbers 1 to 18 have been suggested recently. In this text the 1A to 8A designations will be used.

The horizontal rows of elements in the periodic table are called **periods**. Horizontal row 1 is called the *first period* (it contains H and He); row 2 is called the *second period* (elements Li through Ne); and so on.

We will learn much more about the periodic table as we continue with our study of chemistry. Meanwhile, when an element is introduced in this text, you should always note its position on the periodic table.

2.8 Naming Simple Compounds

When chemistry was an infant science, there was no system for naming compounds. Names such as sugar of lead, blue vitrol, quicklime, Epsom salts, milk of magnesia, gypsum, and laughing gas were coined by early chemists. Such names are called *common names*. As chemistry grew, it became clear that using common names for compounds would lead to unacceptable chaos. Nearly 5 million chemical compounds are currently known. Memorizing common names for these compounds would be an impossible task.

The solution, of course, is to adopt a *system* for naming compounds in which the name tells something about the composition of the compound. After learning the system, a chemist given a formula should be able to name the compound or, given a name, should be able to construct the compound's formula. In this section we will specify the most important rules for naming compounds other than organic compounds (those based on chains of carbon atoms).

We will begin with the systems for naming inorganic **binary compounds**—compounds composed of two elements—which we classify into various types for easier recognition. We will consider both ionic and covalent compounds.

Binary Ionic Compounds (Type I)

Binary ionic compounds contain a positive ion (cation) always written first in the formula and a negative ion (anion). In naming these compounds, the following rules apply:

1. The cation is always named first and the anion second.
2. A monatomic (meaning “one-atom”) cation takes its name from the name of the element. For example, Na^+ is called sodium in the names of compounds containing this ion.
3. A monatomic anion is named by taking the root of the element name and adding *-ide*. Thus the Cl^- ion is called chloride.

Some common monatomic cations and anions and their names are given in Table 2.3.

TABLE 2.3 Common Monatomic Cations and Anions

Cation	Name	Anion	Name
H^+	Hydrogen	H^-	Hydride
Li^+	Lithium	F^-	Fluoride
Na^+	Sodium	Cl^-	Chloride
K^+	Potassium	Br^-	Bromide
Cs^+	Cesium	I^-	Iodide
Be^{2+}	Beryllium	O^{2-}	Oxide
Mg^{2+}	Magnesium	S^{2-}	Sulfide
Ca^{2+}	Calcium	N^{3-}	Nitride
Ba^{2+}	Barium	P^{3-}	Phosphide
Al^{3+}	Aluminum		
Ag^+	Silver		

A monatomic cation has the same name as its parent element.

The rules for naming binary ionic compounds are illustrated by the following examples:

In formulas of ionic compounds, simple ions are represented by the element symbol: Cl means Cl^- , Na means Na^+ , and so on.

Compound	Ions Present	Name
NaCl	Na^+ , Cl^-	Sodium chloride
KI	K^+ , I^-	Potassium iodide
CaS	Ca^{2+} , S^{2-}	Calcium sulfide
Li_3N	Li^+ , N^{3-}	Lithium nitride
CsBr	Cs^+ , Br^-	Cesium bromide
MgO	Mg^{2+} , O^{2-}	Magnesium oxide

SAMPLE EXERCISE 2.3

Naming Type I Binary Compounds

Name each binary compound.

- a. CsF b. AlCl_3 c. LiH

SOLUTION

- a. CsF is cesium fluoride.
 b. AlCl_3 is aluminum chloride.
 c. LiH is lithium hydride.

Notice that, in each case, the cation is named first, and then the anion is named.

See Exercise 2.59.

TABLE 2.4 Common Type II Cations

Ion	Systematic Name
Fe^{3+}	Iron(III)
Fe^{2+}	Iron(II)
Cu^{2+}	Copper(II)
Cu^+	Copper(I)
Co^{3+}	Cobalt(III)
Co^{2+}	Cobalt(II)
Sn^{4+}	Tin(IV)
Sn^{2+}	Tin(II)
Pb^{4+}	Lead(IV)
Pb^{2+}	Lead(II)
Hg^{2+}	Mercury(II)
Hg_2^{2+} *	Mercury(I)
Ag^+	Silver†
Zn^{2+}	Zinc†
Cd^{2+}	Cadmium†

*Note that mercury(I) ions always occur bound together to form Hg_2^{2+} ions.

†Although these are transition metals, they form only one type of ion, and a Roman numeral is not used.

Binary Ionic Compounds (Type II)

In the binary ionic compounds considered above (Type I), the metal present forms only a single type of cation. That is, sodium forms only Na^+ , calcium forms only Ca^{2+} , and so on. However, as we will see in more detail later in the text, there are many metals that form more than one type of positive ion and thus form more than one type of ionic compound with a given anion. For example, the compound FeCl_2 contains Fe^{2+} ions, and the compound FeCl_3 contains Fe^{3+} ions. In a case such as this, the *charge on the metal ion must be specified*. The systematic names for these two iron compounds are iron(II) chloride and iron(III) chloride, respectively, where the *Roman numeral indicates the charge of the cation*.

Another system for naming these ionic compounds that is seen in the older literature was used for metals that form only two ions. *The ion with the higher charge has a name ending in -ic, and the one with the lower charge has a name ending in -ous*. In this system, for example, Fe^{3+} is called the ferric ion, and Fe^{2+} is called the ferrous ion. The names for FeCl_3 and FeCl_2 are then ferric chloride and ferrous chloride, respectively. In this text we will use the system that employs Roman numerals. Table 2.4 lists the systematic names for many common type II cations.

SAMPLE EXERCISE 2.4

Naming Type II Binary Compounds

Give the systematic name of each of the following compounds.

- a. CuCl b. HgO c. Fe_2O_3 d. MnO_2 e. PbCl_2

Type II binary ionic compounds contain a metal that can form more than one type of cation.

A compound must be electrically neutral.

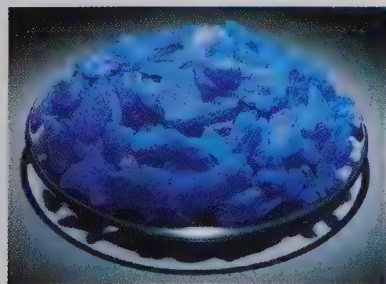
SOLUTION

All these compounds include a metal that can form more than one type of cation; thus we must first determine the charge on each cation. This can be done by recognizing that a compound must be electrically neutral; that is, the positive and negative charges must exactly balance.

- In CuCl , for example, since the anion is Cl^- , the cation must be Cu^+ . The name is copper(I) chloride, where the Roman numeral I indicates the $1+$ charge on Cu^+ .
- In HgO , since the anion is oxide, O^{2-} , the mercury cation must be Hg^{2+} to give a net charge of zero as required. Thus the name is mercury(II) oxide.
- In Fe_2O_3 , the three O^{2-} ions carry a total charge of $6-$, so the two iron cations must carry a total charge of $6+$. Thus each iron ion is Fe^{3+} , and the name is iron(III) oxide.
- In the compound MnO_2 , the cation has a $4+$ charge, and the name is manganese(IV) oxide.
- In PbCl_2 the cation has a $2+$ charge, so the name is lead(II) chloride.

See Exercise 2.60.

A compound containing a transition metal usually requires a Roman numeral in its name.



Crystals of copper(II) sulfate.

Note that the use of a Roman numeral in a systematic name is required only in cases where more than one ionic compound forms between a given pair of elements. This case most commonly occurs for compounds containing transition metals, which often form more than one cation. *Elements that form only one cation do not need to be identified by a Roman numeral.* Common metals that do not require Roman numerals are the Group 1A elements, which form only $1+$ ions; the Group 2A elements, which form only $2+$ ions; and aluminum, which forms only Al^{3+} . The element silver deserves special mention at this point. In virtually all its compounds silver is found as the Ag^+ ion. Therefore, although silver is a transition metal (and can potentially form ions other than Ag^+), silver compounds are usually named without a Roman numeral. Thus AgCl is typically called silver chloride rather than silver(I) chloride, although the latter name is technically correct. Also, a Roman numeral is not used for zinc compounds, since zinc forms only the Zn^{2+} ion.

As shown in Sample Exercise 2.4, when a metal ion is present that forms more than one type of cation, the charge on the metal ion must be determined by balancing the positive and negative charges of the compound. To do this you must be able to recognize the common cations and anions and know their charges (see Tables 2.3 and 2.5).

SAMPLE EXERCISE 2.5

Naming Binary Compounds

Give the systematic name of each of the following compounds.

- a. CoBr_2 b. CaCl_2 c. Al_2O_3 d. CrCl_3

SOLUTION

Compound	Name	Comment
a. CoBr_2	Cobalt(II) bromide	Cobalt is a transition metal; the compound name must have a Roman numeral. The two Br^- ions must be balanced by a Co^{2+} ion.

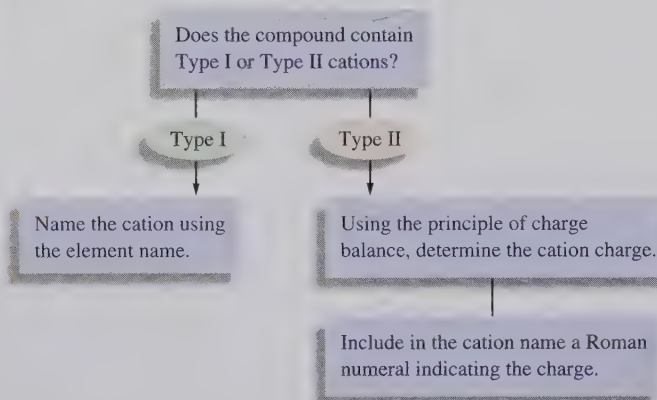
- b. CaCl_2 Calcium chloride Calcium, an alkaline earth metal, forms only the Ca^{2+} ion. A Roman numeral is not necessary.
- c. Al_2O_3 Aluminum oxide Aluminum forms only Al^{3+} . A Roman numeral is not necessary.
- d. CrCl_3 Chromium(III) chloride Chromium is a transition metal. The compound name must have a Roman numeral. CrCl_3 contains Cr^{3+} .

See Exercises 2.61 and 2.62.



Various chromium compounds dissolved in water. From left to right: CrCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{NO}_3)_3$, CrCl_3 , K_2CrO_4 .

The following flowchart is useful when you are naming binary ionic compounds:



The common Type I and Type II ions are summarized in Fig. 2.22. Also shown in Fig. 2.22 are the common monatomic ions.

1A																			8A
	2A									3A	4A	5A	6A	7A					
	Li^+											N^{3-}	O^{2-}	F^-					
	Na^+	Mg^{2+}								Al^{3+}			S^{2-}	Cl^-					
	K^+	Ca^{2+}				Cr^{2+} Cr^{3+}	Mn^{2+} Mn^{3+}	Fe^{2+} Fe^{3+}	Co^{2+} Co^{3+}		Cu^+ Cu^{2+}	Zn^{2+}			Br^-				
	Rb^+	Sr^{2+}									Ag^+	Cd^{2+}		Sn^{2+} Sn^{4+}		I^-			
	Cs^+	Ba^{2+}									Hg_2^{2+} Hg^{2+}		Pb^{2+} Pb^{4+}						

Common Type I cations Common Type II cations Common monatomic anions

FIGURE 2.22
The common cations and anions.

CHEMICAL IMPACT

Buckminsterfullerene: A New Form of Carbon

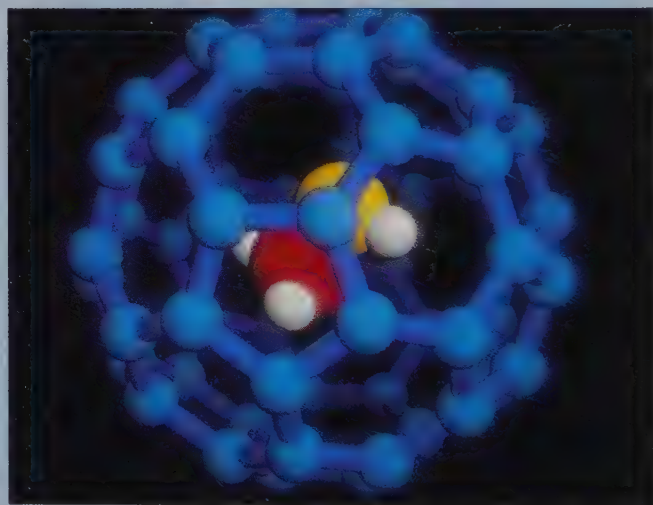
A favorite chemistry exam question—What are the allotropes of elemental carbon?—now has a new answer: diamond, graphite, and buckminsterfullerene. Buckminsterfullerene? This fascinating new form of elemental carbon containing C_{60} molecules was first identified by chemists Richard E. Smalley and Robert F. Curl at Rice University and Harold F. Kroto at the University of Sussex, who were awarded the 1996 Nobel Prize in chemistry for their achievement.

The structure of the C_{60} molecule resembles a soccer ball. It is a spherical molecule with the carbon atoms arranged at the 60 vertices of 32 interconnecting pentagons (12) and hexagons (20). It gets its name from the work of R. Buckminster Fuller, who proposed geodesic domes with frameworks similar to the arrangement of carbons in C_{60} .

Buckminsterfullerene was first synthesized in large quantities in the lab of physicist Donald R. Huffman by vaporizing carbon from pure graphite electrodes in an atmosphere of helium gas at a pressure of 100 torr. The soot that forms in this environment is about 5% C_{60} by mass. The scientists have also found significant quantities of another “fullerene” in this soot that consists of C_{70} molecules. The C_{70} molecule is similar to the spherical C_{60} molecule except that the extra carbon atoms lead to an egg-shaped structure. Experiments also show that when the carbon-60 and -70 fullerenes are subjected to intense laser pulses they open their cages and combine to form huge spherical fullerenes with 400 or more carbon atoms.

The discovery of fullerenes has led to a flurry of activity in labs around the world as chemists rush to characterize this new substance. Scientists have produced the C_{60}^- and C_{60}^{2-} anions and have prepared C_{60} molecules with various substituents added. In addition, many molecules have been synthesized with metal atoms trapped inside the cages. Examples are $La @ C_{60}$, $K @ C_{14}$, and $U @ C_{28}$, where the @ symbol means that the metal is inside the cage.

In a related development, by using synthetic procedures similar to those used to make fullerenes, scientists have discovered carbon nanotubes—long, cylindrical structures composed entirely of carbon atoms in a mesh pattern like chicken wire wound into a cylinder with half a buckminsterfullerene sphere as a cap on the end. The nanotubes can have single walls or can consist of several concentric cylinders. Because the graphite-like (graphene) sheets can be rolled with varying degrees of twist along the length of the nanotubes, many different nanotubes are possible with varying properties. For example, some nanotubes conduct electricity as well as metals, whereas others are insulators. The hope is that these nanotubes can function as tiny wires in molecular-level electronic devices. Carbon nanotubes will almost certainly affect everyone's life in the near future.



A space-filled model of C_{60} containing a “caged” methanol molecule.

Ionic Compounds with Polyatomic Ions

We have not yet considered ionic compounds that contain polyatomic ions. For example, the compound ammonium nitrate, NH_4NO_3 , contains the polyatomic ions NH_4^+ and NO_3^- . Polyatomic ions are assigned special names that *must be memorized* to name the compounds containing them. The most important polyatomic ions and their names are listed in Table 2.5.

Polyatomic ion formulas must be memorized.

TABLE 2.5 Common Polyatomic Ions

Ion	Name	Ion	Name
Hg_2^{2+}	Mercury(I)	NCS^-	Thiocyanate
NH_4^+	Ammonium	CO_3^{2-}	Carbonate
NO_2^-	Nitrite	HCO_3^-	Hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	Nitrate	ClO^-	Hypochlorite
SO_3^{2-}	Sulfite	ClO_2^-	Chlorite
SO_4^{2-}	Sulfate	ClO_3^-	Chlorate
HSO_4^-	Hydrogen sulfate (bisulfate is a widely used common name)	ClO_4^-	Perchlorate
OH^-	Hydroxide	$\text{C}_2\text{H}_3\text{O}_2^-$	Acetate
CN^-	Cyanide	MnO_4^-	Permanganate
PO_4^{3-}	Phosphate	$\text{Cr}_2\text{O}_7^{2-}$	Dichromate
HPO_4^{2-}	Hydrogen phosphate	CrO_4^{2-}	Chromate
H_2PO_4^-	Dihydrogen phosphate	O_2^{2-}	Peroxide
		$\text{C}_2\text{O}_4^{2-}$	Oxalate

Note in Table 2.5 that several series of anions contain an atom of a given element and different numbers of oxygen atoms. These anions are called **oxyanions**. When there are two members in such a series, the name of the one with the smaller number of oxygen atoms ends in *-ite* and the name of the one with the larger number ends in *-ate*—for example, sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}). When more than two oxyanions make up a series, *hypo-* (less than) and *per-* (more than) are used as prefixes to name the members of the series with the fewest and the most oxygen atoms, respectively. The best example involves the oxyanions containing chlorine, as shown in Table 2.5.

SAMPLE EXERCISE 2.6

Naming Compounds Containing Polyatomic Ions

Give the systematic name of each of the following compounds.

- a. Na_2SO_4 b. KH_2PO_4 c. $\text{Fe}(\text{NO}_3)_3$ d. $\text{Mn}(\text{OH})_2$
 e. Na_2SO_3 f. Na_2CO_3 g. NaHCO_3 h. CsClO_4
 i. NaOCl j. Na_2SeO_4 k. KBrO_3

SOLUTION

Compound	Name	Comment
a. Na_2SO_4	Sodium sulfate	
b. KH_2PO_4	Potassium dihydrogen phosphate	
c. $\text{Fe}(\text{NO}_3)_3$	Iron(III) nitrate	Transition metal—name must contain a Roman numeral. Fe^{3+} ion balances three NO_3^- ions.

d. $\text{Mn}(\text{OH})_2$	Manganese(II) hydroxide	Transition metal—name must contain a Roman numeral. Mn^{2+} ion balances two OH^- ions.
e. Na_2SO_3	Sodium sulfite	
f. Na_2CO_3	Sodium carbonate	
g. NaHCO_3	Sodium hydrogen carbonate	Often called sodium bicarbonate.
h. CsClO_4	Cesium perchlorate	
i. NaOCl	Sodium hypochlorite	
j. Na_2SeO_4	Sodium selenate	Atoms in the same group, like sulfur and selenium, often form similar ions that are named similarly. Thus SeO_4^{2-} is selenate, like SO_4^{2-} (sulfate). As above, BrO_3^- is bromate, like ClO_3^- (chlorate).
k. KBrO_3	Potassium bromate	

See Exercises 2.63 and 2.64.

In binary covalent compounds, the element names follow the same rules as for binary ionic compounds.

Binary Covalent Compounds (Type III)

Binary covalent compounds are formed between *two nonmetals*. Although these compounds do not contain ions, they are named very similarly to binary ionic compounds.

In the naming of binary covalent compounds, the following rules apply:

1. The first element in the formula is named first, using the full element name.
2. The second element is named as if it were an anion.
3. Prefixes are used to denote the numbers of atoms present. These prefixes are given in Table 2.6.
4. The prefix *mono-* is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.

To see how these rules apply, we will now consider the names of the several covalent compounds formed by nitrogen and oxygen:

TABLE 2.6 Prefixes Used to Indicate Number in Chemical Names

Prefix	Number Indicated
<i>mono-</i>	1
<i>di-</i>	2
<i>tri-</i>	3
<i>tetra-</i>	4
<i>penta-</i>	5
<i>hexa-</i>	6
<i>hepta-</i>	7
<i>octa-</i>	8
<i>nona-</i>	9
<i>deca-</i>	10

Compound	Systematic Name	Common Name
N_2O	Dinitrogen monoxide	Nitrous oxide
NO	Nitrogen monoxide	Nitric oxide
NO_2	Nitrogen dioxide	
N_2O_3	Dinitrogen trioxide	
N_2O_4	Dinitrogen tetroxide	
N_2O_5	Dinitrogen pentoxide	

Notice from the preceding examples that to avoid awkward pronunciations, we often drop the final *o* or *a* of the prefix when the element begins with a vowel. For example, N_2O_4 is called dinitrogen tetroxide, *not* dinitrogen tetraoxide, and CO is called carbon monoxide, *not* carbon monooxide.

Some compounds are always referred to by their common names. The two best examples are water and ammonia. The systematic names for H_2O and NH_3 are never used.

SAMPLE EXERCISE 2.7

Naming Type III Binary Compounds

Name each of the following compounds.

- a. PCl_5 b. PCl_3 c. SF_6 d. SO_3 e. SO_2 f. CO_2

SOLUTION

Compound	Name
a. PCl_5	Phosphorus pentachloride
b. PCl_3	Phosphorus trichloride
c. SF_6	Sulfur hexafluoride
d. SO_3	Sulfur trioxide
e. SO_2	Sulfur dioxide
f. CO_2	Carbon dioxide

See Exercises 2.65 and 2.66.

The rules for naming binary compounds are summarized in Fig. 2.23. Prefixes to indicate the number of atoms are used only in Type III binary compounds (those containing two nonmetals). An overall strategy for naming compounds is given in Fig. 2.24.

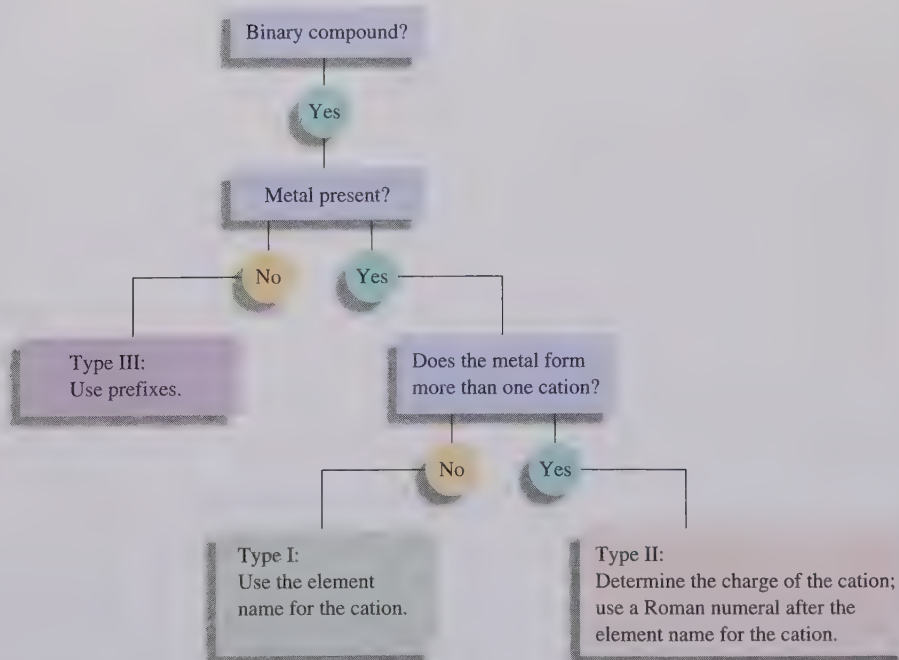


FIGURE 2.23

A flowchart for naming binary compounds.

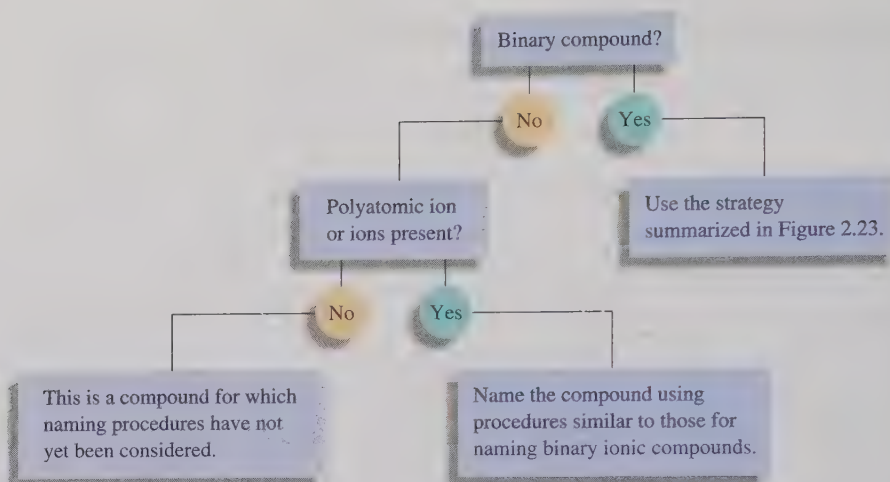


FIGURE 2.24
Overall strategy for naming
chemical compounds.

SAMPLE EXERCISE 2.8

Naming Various Types of Compounds

Give the systematic name for each of the following compounds.

- a. P_4O_{10} b. Nb_2O_5 c. Li_2O_2 d. $\text{Ti}(\text{NO}_3)_4$

SOLUTION

Compound	Name	Comment
a. P_4O_{10}	Tetraphosphorus decaoxide	Binary covalent compound (Type III), so prefixes are used. The <i>a</i> in <i>deca</i> - is sometimes dropped.
b. Nb_2O_5	Niobium(V) oxide	Type II binary compound containing Nb^{5+} and O^{2-} ions. Niobium is a transition metal and requires a Roman numeral.
c. Li_2O_2	Lithium peroxide	Type I binary compound containing the Li^+ and O_2^{2-} (peroxide) ions.
d. $\text{Ti}(\text{NO}_3)_4$	Titanium(IV) nitrate	Not a binary compound. Contains the Ti^{4+} and NO_3^- ions. Titanium is a transition metal and requires a Roman numeral.

See Exercise 2.67.

Formulas from Names

So far we have started with the chemical formula of a compound and decided on its systematic name. The reverse process is also important. For example, given the name calcium hydroxide, we can write the formula as $\text{Ca}(\text{OH})_2$ because we know that calcium forms only Ca^{2+} ions and that, since hydroxide is OH^- , two of these anions will be required to give a neutral compound. Similarly, the name iron(II) oxide implies the formula FeO , since the Roman numeral II indicates the presence of Fe^{2+} , which is balanced by one oxide ion, O^{2-} .

SAMPLE EXERCISE 2.9

Writing Compound Formulas from Names

Given the following systematic names, write the formula for each compound.

- Vanadium(V) fluoride
- Dioxygen difluoride
- Rubidium peroxide
- Gallium oxide

SOLUTION

Name	Chemical Formula	Comment
a. Vanadium(V) fluoride	VF_5	The compound contains V^{5+} ions and requires five F^- ions for charge balance.
b. Dioxygen difluoride	O_2F_2	The prefix <i>di-</i> indicates two of each atom.
c. Rubidium peroxide	Rb_2O_2	Since rubidium is in Group 1A, it forms only $1+$ ions. Thus two Rb^+ ions are needed to balance the $2-$ charge on the peroxide ion (O_2^{2-}).
d. Gallium oxide	Ga_2O_3	Since gallium is in Group 3A, like aluminum, it forms only $3+$ ions. Two Ga^{3+} ions are required to balance the charge on three O^{2-} ions.

See Exercises 2.69 and 2.70.

Acids

When dissolved in water, certain molecules produce a solution containing free H^+ ions (protons). These substances, **acids**, will be discussed in detail in Chapters 4, 14, and 15. Here we will simply present the rules for naming acids.

An acid can be viewed as a molecule with one or more H^+ ions attached to an anion. The rules for naming acids depend on whether the anion contains oxygen. If the anion *does not contain oxygen*, the acid is named with the prefix *hydro-* and the suffix *-ic*. For example, when gaseous HCl is dissolved in water, it forms hydrochloric acid. Similarly, HCN and H_2S dissolved in water are called hydrocyanic and hydrosulfuric acids, respectively.

When the anion *contains oxygen*, the acidic name is formed from the root name of the anion with a suffix of *-ic* or *-ous*, depending on the name of the anion.

- If the anion name ends in *-ate*, the suffix *-ic* is added to the root name. For example, H_2SO_4 contains the sulfate anion (SO_4^{2-}) and is called sulfuric acid; H_3PO_4 contains the phosphate anion (PO_4^{3-}) and is called phosphoric acid; and $\text{HC}_2\text{H}_3\text{O}_2$ contains the acetate ion ($\text{C}_2\text{H}_3\text{O}_2^-$) and is called acetic acid.
- If the anion has an *-ite* ending, the *-ite* is replaced by *-ous*. For example, H_2SO_3 , which contains sulfite (SO_3^{2-}), is named sulfurous acid; and HNO_2 , which contains nitrite (NO_2^-), is named nitrous acid.

The application of these rules can be seen in the names of the acids of the oxyanions of chlorine:

Acids can be recognized by the hydrogen that appears first in the formula.

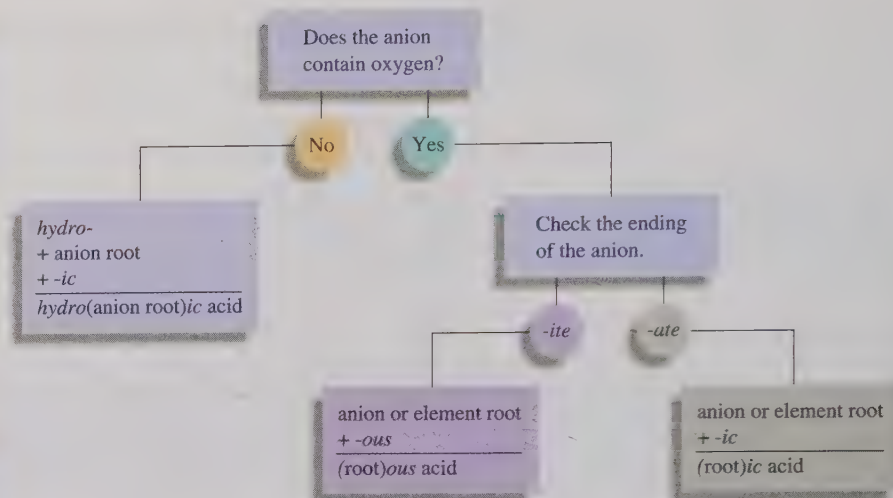
TABLE 2.7 Names of Acids*
That Do Not Contain Oxygen

Acid	Name
HF	Hydrofluoric acid
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HI	Hydroiodic acid
HCN	Hydrocyanic acid
H ₂ S	Hydrosulfuric acid

*Note that these acids are aqueous solutions containing these substances.

TABLE 2.8 Names of Some
Oxygen-Containing Acids

Acid	Name
HNO ₃	Nitric acid
HNO ₂	Nitrous acid
H ₂ SO ₄	Sulfuric acid
H ₂ SO ₃	Sulfurous acid
H ₃ PO ₄	Phosphoric acid
HC ₂ H ₃ O ₂	Acetic acid

**FIGURE 2.25**

A flowchart for naming acids. An acid is best considered as one or more H⁺ ions attached to an anion.

Acid	Anion	Name
HClO ₄	Perchlorate	Perchloric acid
HClO ₃	Chlorate	Chloric acid
HClO ₂	Chlorite	Chlorous acid
HClO	Hypochlorite	Hypochlorous acid

The names of the most important acids are given in Tables 2.7 and 2.8. An overall strategy for naming acids is shown in Fig. 2.25.

For Review

Summary

Three fundamental laws formed the basis for early chemistry: the law of conservation of mass (matter can be neither created nor destroyed), the law of definite proportion (a given compound always contains exactly the same proportion of elements by mass), and the law of multiple proportions (if two elements *A* and *B* form a series of compounds, the ratios of the masses of *A* that combine with 1 gram of *B* can always be represented by small whole numbers). Dalton accounted for these laws in his atomic theory. He postulated that all elements are composed of atoms; that all atoms of a given element are identical; that chemical compounds are formed when atoms combine; and that the atoms themselves are not changed in a chemical reaction but the way they are grouped (bound together) is changed.

Key Terms

Section 2.2

law of conservation of mass
law of definite proportion
law of multiple proportions

Section 2.3

atomic masses
atomic weights
Avogadro's hypothesis

Section 2.4

cathode-ray tube
electron
radioactivity
nuclear atom
nucleus

Section 2.5

proton
neutron
isotopes
atomic number
mass number

Section 2.6

chemical bond
covalent bond
molecule
chemical formula
structural formula
space-filling model
ball-and-stick model
ion
cation
anion
ionic bond
ionic solid (salt)
polyatomic ion

Section 2.7

periodic table
metal
nonmetal
group (family)
alkali metals
alkaline earth metals
halogens
noble gases
period

Section 2.8

binary compounds
binary ionic compounds
oxyanions
binary covalent compounds
acid

Atoms consist of a dense nucleus containing protons and neutrons, surrounded by electrons that occupy a very large volume relative to the size of the nucleus. Electrons have a relatively small mass (1/1840 of the proton mass) and a negative charge. Protons have a positive charge equal in magnitude (but opposite in sign) to that on the electron. A neutron has virtually the same mass as a proton but no charge.

Isotopes are atoms with the same number of protons (thus constituting the same element) but different numbers of neutrons. That is, isotopes have the same atomic number but different mass numbers (total numbers of neutrons and protons).

Atoms can combine to form molecules by sharing electrons to form covalent bonds. A molecule can be described by a chemical formula showing the numbers and types of atoms involved, by a structural formula (showing which atoms are joined to each other), or by ball-and-stick or space-filling models that show the exact positions of the atoms in space. When an atom loses one or more electrons, it forms a positive ion called a cation. If an atom gains electrons, it becomes a negatively charged anion. The interaction of oppositely charged ions to form an ionic compound is called ionic bonding.

The periodic table arranges the elements in order of increasing atomic number, and elements that have similar chemical properties fall into vertical columns, or groups. Most of the elements are metals, which tend to form cations in ionic compounds with nonmetals. Nonmetals tend to form anions when they react with metals.

Compounds are named using systems of rules. These rules vary depending on the type of compound being named. For binary ionic compounds (those which contain a metal and a nonmetal), the metal is named first, followed by a name derived from the root name of the nonmetal. In a compound (Type I) containing a metal that always forms the same cation (sodium always forms Na^+ , magnesium always forms Mg^{2+} , and so on), the name of the metal is sufficient. In a compound (Type II) that contains a metal that can form more than one cation (iron can form Fe^{2+} and Fe^{3+} , and so on), the metal name is followed by a Roman numeral that indicates the cation charge.

Polyatomic ions have special names that must be memorized along with their net charges. In compounds containing polyatomic ions, the cation name is given first, followed by the anion name. For Type III binary covalent compounds (those that contain two nonmetals), the first element is named using the entire element name and the second element is named as if it were an anion. Prefixes are used to indicate the numbers of atoms present.

Suggested Reading

1. Isaac Asimov, *A Short Story of Chemistry* (New York: Anchor Books, Doubleday and Co., Inc., 1965).
2. Robert P. Crease and Charles C. Mann, *The Second Creation*, Chapters 1 and 2 (New York: Macmillan Publishing Co., 1986).
3. Enid S. Lipeles, "The chemical contributions of Amadeo Avogadro," *J. Chem. Ed.* **60** (1983): 127.
4. Sir William Roscoe, *John Dalton and the Rise of Modern Chemistry*, 1896.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

- Which of the following is true about an individual atom? Explain.
 - An individual atom should be considered to be a solid.
 - An individual atom should be considered to be a liquid.
 - An individual atom should be considered to be a gas.
 - The state of the atom depends on which element it is.
 - An individual atom cannot be considered to be a solid, liquid, or gas.

Justify your choice, and for choices you did not pick, explain what is wrong with them.

- You have gone back in time and are working with Dalton. He is working on a table of relative masses, and these are his data:

0.602 g gas A reacts with 0.295 g gas B

0.172 g gas B reacts with 0.401 g gas C

0.320 g gas A reacts with 0.374 g gas C

- Assuming simplest formulas (AB, BC, and AC), construct a table of relative masses for Dalton.

Knowing some history of chemistry, you tell Dalton that if he finds the volumes of the gases at equal temperature and pressure, he need not assume simplest formulas. You collect the following data:

6 volumes gas A + 1 volume gas B $\rightarrow$ 4 volumes product

1 volume gas B + 4 volumes gas C $\rightarrow$ 4 volumes product

3 volumes gas A + 2 volumes gas C $\rightarrow$ 6 volumes product

- Write out the simplest balanced equations, and find the actual relative masses of the elements. Explain your reasoning.
- How would you go about finding the number of “chalk molecules” it takes to write your name on the board? Provide an explanation of all you would need to do and a sample calculation.
 - These questions concern the work of J. J. Thomson.
 - From Thomson’s work, which particles do you think he would feel are most important for the formation of compounds (chemical changes) and why?
 - Of the remaining two subatomic particles, which do you place second in importance for forming compounds and why?
 - Propose three models that explain Thomson’s findings and evaluate them. To be complete you should include Thomson’s findings.
 - Heat is applied to an ice cube in a closed container until only steam is present. Draw a representation of this process, assuming you can see it at an extremely high level of magnification. What happens to the size of the molecules? What happens to the total mass of the sample?

- You have a chemical in a sealed glass container filled with air. The setup is sitting on a balance as shown below. The chemical is ignited by means of a magnifying glass focusing sunlight on the reactant. After the chemical has completely burned, which of the following is true? Explain your answer.



- The balance will read less than 250.0 g.
 - The balance will read 250.0 g.
 - The balance will read greater than 250.0 g.
 - Cannot be determined without knowing the identity of the chemical.
- You take three compounds consisting of two elements and decompose them. To determine the relative masses of X, Y, and Z, you collect and weigh the elements, obtaining the following data:

Elements in Compound	Masses of Elements
X and Y	X = 0.4 g, Y = 4.2 g
Y and Z	Y = 1.4 g, Z = 1.0 g
X and Y	X = 2.0 g, Y = 7.0 g

- What are the assumptions in solving this problem?
 - What are the relative masses of X, Y, and Z?
 - What are the chemical formulas of the three compounds?
 - If you decompose 21 g of compound XY, how much of each element is present?
- The vitamin niacin (nicotinic acid, $C_6H_5NO_2$) can be isolated from a variety of natural sources such as liver, yeast, milk, and whole grain. It also can be synthesized from commercially available materials. Which source of nicotinic acid, from a nutritional view, is best for use in a multivitamin tablet? Why?
 - One of the best indications of a useful theory is that it raises more questions for further experimentation than it originally answered. Does this apply to Dalton’s atomic theory? Give examples.
 - Dalton assumed that all atoms of the same element were identical in all their properties. Explain why this assumption is not valid.
 - Evaluate each of the following as an acceptable name for water:
 - dihydrogen oxide
 - hydroxide hydride
 - hydrogen hydroxide
 - oxygen dihydride
 - Why do we call $Ba(NO_3)_2$ barium nitrate, but we call $Fe(NO_3)_2$ iron(II) nitrate?

13. Why is calcium dichloride not the correct systematic name for CaCl_2 ?
14. The common name for NH_3 is ammonia. What would be the systematic name for NH_3 ? Support your answer.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

15. Use Dalton's atomic theory to account for each of the following.
- the law of conservation of mass
 - the law of definite proportion
 - the law of multiple proportions
16. What refinements had to be made in Dalton's atomic theory to account for Gay-Lussac's results on the combining volumes of gases?
17. What evidence led to the conclusion that cathode rays had a negative charge?
18. What discoveries were made by J. J. Thomson, Henri Becquerel, and Lord Rutherford? How did Dalton's model of the atom have to be modified to account for these discoveries?
19. Do the proton and the neutron have exactly the same mass? How do the masses of the proton and the neutron compare to the mass of the electron? Which particles make the greatest contribution to the mass of an atom? Which particles make the greatest contribution to the chemical properties of an atom?
20. Consider Ernest Rutherford's alpha-particle bombardment experiment illustrated in Figure 2.12. How did the results of this experiment lead Rutherford away from the plum pudding model of the atom to propose the nuclear model of the atom?
21. What is the distinction between atomic number and mass number? Between mass number and atomic mass?
22. Distinguish between the terms *family* and *period* in connection with the periodic table. For which of these terms is the term *group* also used?
23. When hydrogen is burned in oxygen to form water, the composition of water formed does not depend on the amount of oxygen reacted. Interpret this in terms of the law of definite proportions.
24. The two most reactive families of elements are the halogens and the alkali metals. How do they differ in their reactivities?

- a. How is this result interpreted in terms of the law of definite proportion?
- b. When a volume of H_2 reacts with an equal volume of Cl_2 at the same temperature and pressure, what volume of product having the formula HCl is formed?
26. A reaction of 1 liter of chlorine gas (Cl_2) with 3 liters of fluorine gas (F_2) yields 2 liters of a gaseous product. All gas volumes are at the same temperature and pressure. What is the formula of the gaseous product?
27. Several compounds containing only sulfur (S) and fluorine (F) are known. Three of them have the following compositions:
- 1.188 g of F for every 1.000 g of S
 - 2.375 g of F for every 1.000 g of S
 - 3.563 g of F for every 1.000 g of S
- How do these data illustrate the law of multiple proportions?
28. Hydrazine, ammonia, and hydrogen azide all contain only nitrogen and hydrogen. The mass of hydrogen that combines with 1.00 g of nitrogen for each compound is 1.44×10^{-1} g, 2.16×10^{-1} g, and 2.40×10^{-2} g, respectively. Show how these data illustrate the law of multiple proportions.
29. Early tables of atomic weights (masses) were generated by measuring the mass of a substance that reacts with 1.00 g of oxygen. Given the following data and taking the atomic mass of hydrogen as 1.00, generate a table of relative atomic masses for oxygen, sodium, and magnesium.

Element	Mass That Combines	
	with 1.00 g Oxygen	Assumed Formula
Hydrogen	0.126 g	HO
Sodium	2.875 g	NaO
Magnesium	1.500 g	MgO

How do your values compare with those in the periodic table? How do you account for any differences?

30. Indium oxide contains 4.784 g of indium for every 1.000 g of oxygen. In 1869, when Mendeleev first presented his version of the periodic table, he proposed the formula In_2O_3 for indium oxide. Before that time it was thought that the formula was InO . What values for the atomic mass of indium are obtained using these two formulas? Assume that oxygen has an atomic mass of 16.00.

Exercises

In this section similar exercises are paired.

Development of the Atomic Theory

25. When mixtures of gaseous H_2 and gaseous Cl_2 react, a product forms that has the same properties regardless of the relative amounts of H_2 and Cl_2 used.

The Nature of the Atom

31. From the information in this chapter on the mass of the proton, the mass of the electron, and the sizes of the nucleus and the atom, calculate the densities of a hydrogen nucleus and a hydrogen atom.
32. If you wanted to make an accurate scale model of the hydrogen atom and decided that the nucleus would have a diameter of 1 mm, what would be the diameter of the entire model?

33. In an experiment it was found that the total charge on an oil drop was 5.93×10^{-18} C. How many negative charges does the drop contain?

34. A chemist in a galaxy far, far away performed the Millikan oil drop experiment and got the following results for the charges on various drops. Use these data to calculate the charge of the electron in zirkombs.

$$\begin{array}{ll} 2.56 \times 10^{-12} \text{ zirkombs} & 7.68 \times 10^{-12} \text{ zirkombs} \\ 3.84 \times 10^{-12} \text{ zirkombs} & 6.40 \times 10^{-13} \text{ zirkombs} \end{array}$$

35. What are the symbols of the following metals: sodium, beryllium, manganese, chromium, uranium?

36. What are the symbols of the following nonmetals: fluorine, chlorine, bromine, sulfur, oxygen, phosphorus?

37. Give the names of the metals that correspond to the following symbols: Sn, Pt, Co, Ni, Mg, Ba, K.

38. Give the names of the nonmetals that correspond to the following symbols: As, I, Xe, He, C, Si.

39. List the noble gas elements. Which of the noble gases has only radioactive isotopes? (This situation is indicated on most periodic tables by parentheses around the mass of the element. See inside front cover.)

40. Which lanthanide element and which transition element have only radioactive isotopes? (See Exercise 39.)

41. In the periodic table, how many elements are found in

- a. the second period? c. the fourth period?
b. the third period? d. Group 5A?

42. In the periodic table, how many elements are found in

- a. Group 2A? c. the nickel group?
b. the oxygen family? d. Group 8A?

43. Give the number of protons and neutrons in the nucleus of each of the following atoms:

- a. $^{238}_{94}\text{Pu}$ d. ^4_2He
b. $^{65}_{29}\text{Cu}$ e. $^{60}_{27}\text{Co}$
c. $^{52}_{24}\text{Cr}$ f. $^{54}_{24}\text{Cr}$

44. How many protons and neutrons are in the nucleus of each of the following atoms? In a neutral atom of each element, how many electrons are present?

- a. $^{79}_{35}\text{Br}$ d. $^{133}_{55}\text{Cs}$
b. $^{81}_{35}\text{Br}$ e. ^3_1H
c. $^{239}_{94}\text{Pu}$ f. $^{56}_{26}\text{Fe}$

45. Write the atomic symbol (^A_ZX) for each of the atoms described below.

- a. $Z = 5$, $A = 12$
b. the isotope with 7 protons and 8 neutrons in its nucleus
c. atomic number = 17, number of neutrons = 18
d. $Z = 92$, number of neutrons = 143
e. number of protons = 6, mass number = 14
f. the isotope of phosphorus with 16 neutrons in its nucleus

46. Write the atomic symbol (^A_ZX) for each of the following isotopes.

- a. $Z = 8$, number of neutrons = 9
b. the isotope of chlorine in which $A = 37$
c. $Z = 27$, $A = 60$
d. number of protons = 26, number of neutrons = 31
e. the isotope of I with a mass number of 131
f. $Z = 3$, number of neutrons = 4

47. What is the symbol for an ion with 63 protons, 60 electrons, and 88 neutrons? If an ion contains 50 protons, 68 neutrons, and 48 electrons, what is its symbol?

48. What is the symbol of an ion with 16 protons, 18 neutrons, and 18 electrons? What is the symbol for an ion that has 16 protons, 16 neutrons, and 18 electrons?

49. Complete the following table:

Symbol	Number of Protons in Nucleus	Number of Neutrons in Nucleus	Number of Electrons	Net Charge
	33	42		3+
$^{128}_{52}\text{Te}^{2-}$			54	
	16	16	16	
	81	123		1+
$^{195}_{78}\text{Pt}$				

50. Complete the following table:

Symbol	Number of Protons in Nucleus	Number of Neutrons in Nucleus	Number of Electrons	Net Charge
$^{238}_{92}\text{U}$				
	20	20		2+
	23	28	20	
$^{89}_{39}\text{Y}$				
	35	44	36	
	15	16		3-

51. Classify the following elements as metals or nonmetals:

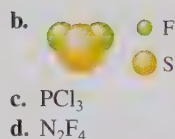
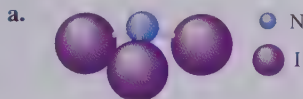
Mg	Si	Rn
Ti	Ge	Eu
Au	B	Am
Bi	At	Br

52. The distinction between metals and nonmetals is really not a clear one. Some elements, called *metalloids*, are intermediate in their properties. Which elements in Exercise 51 would you reclassify as metalloids? What other elements in the periodic table would you expect to be metalloids?

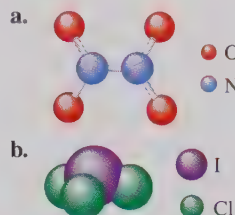
53. Which of the following sets of elements are all in the same group in the periodic table?
- a. Fe, Ru, Os c. Sn, As, S
b. Rh, Pd, Ag d. Se, Te, Po
54. For each of the following sets of elements, label each as either noble gases, halogens, alkali metals, alkaline earth metals, or transition metals.
- a. Ti, Fe, Ag d. Ne, Kr, Xe
b. Mg, Sr, Ba e. F, Br, I
c. Li, K, Rb
55. Consider the elements of Group 4A (the "carbon family"): C, Si, Ge, Sn, and Pb. What is the trend in metallic character as one goes down this group?
56. What is the trend in metallic character going from left to right across a period in the periodic table?
57. Would you expect each of the following atoms to gain or lose electrons when forming ions? What ion is the most likely in each case?
- a. Na c. Ba e. Al
b. Sr d. I f. S
58. Would you expect each of the following atoms to gain or lose electrons when forming ions? What ion is the most likely in each case?
- a. Ra c. P e. Br
b. In d. Te f. Rb

Nomenclature

59. Name each of the following compounds:
- a. NaCl c. CaS
b. Rb₂O d. AlI₃
60. Name each of the following compounds:
- a. Hg₂O c. CoS
b. FeBr₃ d. TiCl₄
61. Name each of the following compounds:
- a. CrO₃ c. Al₂O₃ e. CaBr₂
b. Cr₂O₃ d. NaH f. ZnCl₂
62. Name each of the following compounds:
- a. CsF c. Ag₂S e. TiO₂
b. Li₃N d. MnO₂ f. Sr₃P₂
63. Name each of the following compounds:
- a. KClO₄ c. Al₂(SO₄)₃
b. Ca₃(PO₄)₂ d. Pb(NO₃)₂
64. Name each of the following compounds:
- a. BaSO₃ c. KMnO₄
b. NaNO₂ d. K₂Cr₂O₇
65. Name each of the following compounds:



66. Name each of the following compounds:



- c. SO₂
d. P₂S₅

67. Name each of the following compounds:

- a. CuI f. S₄N₄
b. CuI₂ g. SF₆
c. CoI₂ h. NaOCl
d. Na₂CO₃ i. BaCrO₄
e. NaHCO₃ j. NH₄NO₃

68. Name each of the following compounds:

- a. HC₂H₃O₂ g. H₂SO₄
b. NH₄NO₂ h. Sr₃N₂
c. Co₂S₃ i. Al₂(SO₃)₃
d. ICl j. SnO₂
e. Pb₃(PO₄)₂ k. Na₂CrO₄
f. KIO₃ l. HClO

69. Write the formula for each of the following compounds:

- a. cesium bromide e. silicon tetrachloride
b. barium sulfate f. chlorine trifluoride
c. ammonium chloride g. beryllium oxide
d. chlorine monoxide h. magnesium fluoride

70. Write the formula for each of the following compounds:

- a. sulfur difluoride
b. sulfur hexafluoride
c. sodium dihydrogen phosphate
d. lithium nitride
e. chromium(III) carbonate
f. tin(II) fluoride
g. ammonium acetate
h. ammonium hydrogen sulfate
i. cobalt(III) nitrate k. potassium chlorate
j. mercury(I) chloride l. sodium hydride

71. Write the formula for each of the following compounds:

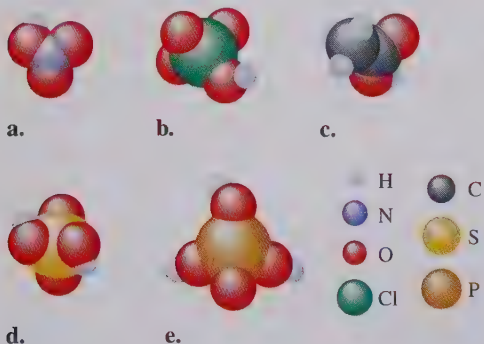
- a. sodium oxide h. copper(I) chloride
b. sodium peroxide i. gallium arsenide
c. potassium cyanide j. cadmium selenide
d. copper(II) nitrate k. zinc sulfide
e. selenium tetrabromide l. nitrous acid
f. lead(II) sulfide m. diphosphorus pentoxide
g. lead(IV) sulfide

72. Write the formula for each of the following compounds:

- ammonium hydrogen phosphate
- mercury(I) sulfide
- silicon dioxide
- sodium sulfite
- aluminum hydrogen sulfate
- nitrogen trichloride
- hydrobromic acid
- bromous acid
- perbromic acid
- potassium hydrogen sulfide
- calcium iodide
- cesium perchlorate

Additional Exercises

73. Chlorine has two natural isotopes: $^{37}_{17}\text{Cl}$ and $^{35}_{17}\text{Cl}$. Hydrogen reacts with chlorine to form the compound HCl. Would a given amount of hydrogen react with different masses of the two chlorine isotopes? Does this conflict with the law of definite proportion? Why or why not?
74. Technetium (Tc) was the first synthetically produced element. Technetium comes from the Greek word for “artificial”. It was first produced by Perries and Segre in 1937 in Berkeley, California, by bombarding a molybdenum plate with ^2H nuclei. Elemental technetium is produced from ammonium pertechnetate. How many protons and neutrons are in the nuclei of ^{98}Tc and ^{99}Tc ? What is the formula of ammonium pertechnetate?
75. Name the following acids illustrated below.



76. For each of the following ions, indicate the total number of protons and electrons in the ion. For the positive ions in the list, predict the formula of the simplest compound formed between each positive ion and the oxide ion. For the negative ions in the list, predict the formula of the simplest compound formed between each negative ion and the aluminum ion.

- Fe^{2+}
- Fe^{3+}
- Ba^{2+}
- Cs^{+}
- S^{2-}
- P^{3-}
- Br^{-}
- N^{3-}

77. The formulas and common names for several substances are given below. Give the systematic names for these substances.

- sugar of lead $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
- blue vitrol CuSO_4
- quicklime CaO
- Epsom salts MgSO_4
- milk of magnesia $\text{Mg}(\text{OH})_2$
- gypsum CaSO_4
- laughing gas N_2O

78. Identify each of the following elements:

- a member of the same family as oxygen whose most stable ion contains 54 electrons
- a member of the alkali metal family whose most stable ion contains 36 electrons
- a noble gas with 18 protons in the nucleus
- a halogen with 85 protons and 85 electrons

79. How many hydrogen atoms are there in 1 molecule of $\text{C}_6\text{H}_{12}\text{O}_6$? in 2 molecules of C_2H_6 ? in 3 molecules of CH_4 ? in 4 molecules of H_3PO_4 ? in 6 molecules of H_2O ?

80. An element's most stable ion forms an ionic compound with bromine, having the formula XBr_2 . If the ion of element X has a mass number of 230 and has 86 electrons, what is the identity of the element, and how many neutrons does it have?

81. The designations 1A through 8A used for certain families of the periodic table are helpful for predicting the charges on ions in binary ionic compounds. In these compounds, the metals generally take on a positive charge equal to the family number, while the nonmetals take on a negative charge equal to the family number minus eight. Thus the compound between sodium and chlorine contains Na^{+} ions and Cl^{-} ions and has the formula NaCl. Predict the formula and the name of the binary compound formed from the following pairs of elements.

- Ca and N
- K and O
- Rb and F
- Mg and S
- Ba and I
- Al and Se
- Cs and P
- In and Br

82. By analogy with phosphorous compounds, name the following: Na_3AsO_4 , H_3AsO_4 , $\text{Mg}_3(\text{SbO}_4)_2$.

Challenge Problems

83. The elements in one of the groups in the periodic table are often called the **coinage metals**. Identify the elements in this group based on your own experience.

84. A combustion reaction involves the reaction of a substance with oxygen gas. The complete combustion of any hydrocarbon (binary compound of carbon and hydrogen) produces carbon dioxide and water as the only products. Octane is a hydrocarbon that is found in gasoline. Complete combustion of octane produces 8 liters of carbon dioxide for every 9 liters of water vapor (both measured at the same temperature and

pressure). What is the ratio of carbon atoms to hydrogen atoms in a molecule of octane?

85. Two elements, R and Q, combine to form two binary compounds. In the first compound, 14.0 g of R combines with 3.00 g of Q. In the second compound, 7.00 g of R combines with 4.50 g of Q. Show that these data are in accord with the law of multiple proportions. If the formula of the second compound is RQ, what is the formula of the first compound?
86. The early alchemists used to do an experiment in which water was boiled for several days in a sealed glass container. Eventually, some solid residue would appear in the bottom of the flask, which was interpreted to mean that some of the water in the flask had been converted into "earth." When Lavoisier repeated this experiment, he found that the water weighed the same before and after heating and the mass of the flask plus the solid residue equaled the original mass of the flask. Were the alchemists correct? Explain what really happened. (This experiment is described in the article by A. F. Scott in *Scientific American*, January 1984.)
87. Each of the following statements is true, but Dalton might have had trouble explaining some of them with his atomic theory. Give explanations for the following statements.
- a. The space-filling models for ethyl alcohol and dimethyl ether are shown below.



These two compounds have the same composition by mass (52% carbon, 13% hydrogen, and 35% oxygen), yet the two have different melting points, boiling points, and solubilities in water.

- b. Burning wood leaves an ash that is only a small fraction of the mass of the original wood.
- c. Atoms can be broken down into smaller particles.
- d. One sample of lithium hydride is 87.4% lithium by mass, while another sample of lithium hydride is 74.9% lithium by mass. However, the two samples have the same properties.



Media Activities

1. Many early scientists performed experiments to determine the structure of the atom. J.J. Thomson's work with cathode-ray tubes led to the discovery of electrons. Open the Cathode Ray Tube Visualization to review cathode rays and the effect of a magnet on these rays.
2. There are many ways to represent structures of compounds. The Molecule Library on the student web site shows various representations of molecules referenced in each chapter. Choose CH_4 from the Molecule Library. A wireframe representation of CH_4 comes up initially; however, you can change this to other types of representations. Go to Display to see the other options. Click on each type of representation (for example, Sticks, Spacefill, Ball and Stick) to see what they look like. You can also enhance the display by clicking Options. For each representation, try various options. Note that nothing happens when you select Labels. This option only labels atoms other than carbon and hydrogen. Since CH_4 is only composed of C and H, no labels appear. Choose some more molecules and play.
3. Test your understanding of Chapter 2 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Stoichiometry

3

Chemical reactions have a profound effect on our lives. There are many examples: Food is converted to energy in the human body; nitrogen and hydrogen are combined to form ammonia, which is used as a fertilizer; fuels and plastics are produced from petroleum; the starch in plants is synthesized from carbon dioxide and water using energy from sunlight; human insulin is produced in laboratories by bacteria; cancer is induced in humans by substances from our environment; and so on, in a seemingly endless list. The central activity of chemistry is to understand chemical changes such as these, and the study of reactions occupies a central place in this book. We will examine why reactions occur, how fast they occur, and the specific pathways they follow.

In this chapter we will consider the quantities of materials consumed and produced in chemical reactions. This area of study is called **chemical stoichiometry** (pronounced stoy·kē·om'·etry). To understand chemical stoichiometry, you must first understand the concept of relative atomic masses.

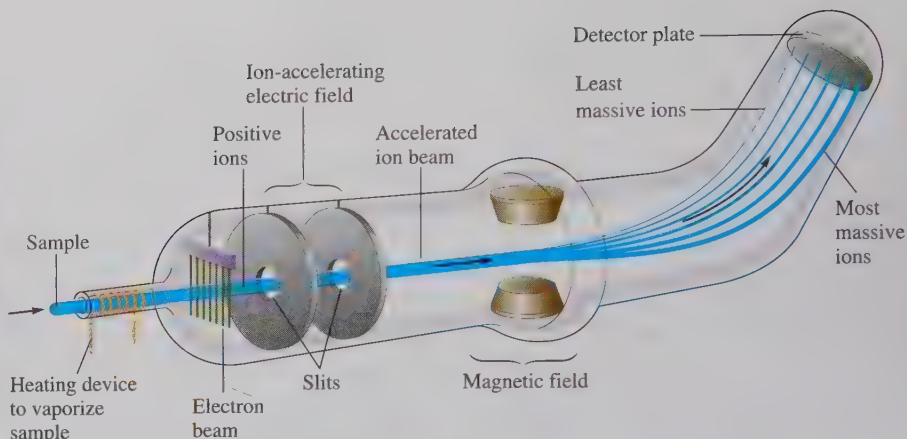
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- 3.3 Molar Mass
- 3.4 Percent Composition of Compounds
- 3.5 Determining the Formula of a Compound
- 3.6 Chemical Equations
 - Chemical Reactions
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- 3.7 Balancing Chemical Equations
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- 3.9 Calculations Involving a Limiting Reactant

3.1 Atomic Masses

As we saw in Chapter 2, the first quantitative information about atomic masses came from the work of Dalton, Gay-Lussac, Lavoisier, Avogadro, and Berzelius. By observing the proportions in which elements combine to form various compounds, nineteenth-century chemists calculated relative atomic masses. The modern system of atomic masses, instituted in 1961, is based on ^{12}C ("carbon twelve") as the standard. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass units (amu), and the masses of all other atoms are given relative to this standard.

The violent chemical reaction of bromine and phosphorus.

**FIGURE 3.1**

(left) A scientist injecting a sample into a mass spectrometer. (above) Schematic diagram of a mass spectrometer.

The most accurate method currently available for comparing the masses of atoms involves the use of the **mass spectrometer**. In this instrument, diagramed in Fig. 3.1, atoms or molecules are passed into a beam of high-speed electrons, which knock electrons off the atoms or molecules being analyzed and change them into positive ions. An applied electric field then accelerates these ions into a magnetic field. Because an accelerating ion produces its own magnetic field, an interaction with the applied magnetic field occurs, which tends to change the path of the ion. The amount of path deflection for each ion depends on its mass—the most massive ions are deflected the smallest amount—which causes the ions to separate, as shown in Fig. 3.1. A comparison of the positions where the ions hit the detector plate gives very accurate values of their relative masses. For example, when ^{12}C and ^{13}C are analyzed in a mass spectrometer, the ratio of their masses is found to be

$$\frac{\text{Mass } ^{13}\text{C}}{\text{Mass } ^{12}\text{C}} = 1.0836129$$

Since the atomic mass unit is defined such that the mass of ^{12}C is *exactly* 12 atomic mass units, then on this same scale,

$$\text{Mass of } ^{13}\text{C} = (1.0836129)(12 \text{ amu}) = 13.003355 \text{ amu}$$

↑
 Exact number
 by definition

The masses of other atoms can be determined in a similar fashion.

The mass for each element is given in the table inside the front cover of this text. This value, even though it is actually a mass, is (for historical reasons) sometimes called the *atomic weight* for each element.

Look at the value of the atomic mass of carbon given in this table. You might expect to see 12, since we said the system of atomic masses is based on ^{12}C . However, the number given for carbon is not 12 but 12.01. Why? The reason for this apparent discrepancy is that the carbon found on earth (natural carbon) is a mixture

Most elements occur in nature as mixtures of isotopes; thus atomic masses are usually average values.



It is much easier to weigh out 600 hex nuts than count them one by one.

of the isotopes ^{12}C , ^{13}C , and ^{14}C . All three isotopes have six protons, but they have six, seven, and eight neutrons, respectively. Because natural carbon is a mixture of isotopes, the atomic mass we use for carbon is an *average value* reflecting the average of the isotopes composing it.

The average atomic mass for carbon is computed as follows: It is known that natural carbon is composed of 98.89% ^{12}C atoms and 1.11% ^{13}C atoms. The amount of ^{14}C is negligibly small at this level of precision. Using the masses of ^{12}C (exactly 12 amu) and ^{13}C (13.003355 amu), we can calculate the average atomic mass for natural carbon as follows:

$$98.89\% \text{ of } 12 \text{ amu} + 1.11\% \text{ of } 13.0034 \text{ amu} = (0.9889)(12 \text{ amu}) + (0.0111)(13.0034 \text{ amu}) = 12.01 \text{ amu}$$

This average atomic mass traditionally has been called the *atomic weight* of carbon. In this text we will call the average mass for an element the **average atomic mass** or, simply, the *atomic mass* for that element.

Even though natural carbon does not contain a single atom with mass 12.01, for stoichiometric purposes, we can consider carbon to be composed of only one type of atom with a mass of 12.01. This enables us to count atoms of natural carbon by weighing a sample of carbon.

To make sure that the idea of counting objects by weighing them is clear, consider the following situation. Suppose you work in a hardware store and someone comes in and requests 600 quarter-inch hex nuts. You could count out the nuts, but this would be a slow process. You have a scale available, and you realize that weighing out the nuts would be a much faster means of counting them. What information do you need to count the hex nuts by weighing them? The answer is *the average mass*. To determine the average mass of the nuts, you count out a sample of 10 and weigh them. Suppose the mass of the 10 nuts is 105 g. This result means the average mass of a nut is

$$\frac{105 \text{ g}}{10 \text{ nuts}} = 10.5 \text{ g/nut}$$

Now what size sample will contain 600 hex nuts? It's just

$$600 \text{ nuts} \times \frac{10.5 \text{ g}}{\text{nut}} = 6300 \text{ g} = 6.30 \text{ kg}$$

Therefore, you weigh out a sample of 6.30 kg of the hex nuts, put them in a bag, and assure the customer that the bag contains 600 hex nuts as requested.

Notice that counting by weighing works if you know the *average* mass of the units being counted. In the preceding example, it's possible that not one of the hex nuts had a mass of exactly 10.5 g. All that matters is that the average mass is 10.5 g.

Counting by weighing works just the same for atoms as for hex nuts. For natural carbon with an average mass of 12.01 atomic mass units, to obtain 1000 atoms would require weighing out 12,010 atomic mass units of natural carbon (a mixture of ^{12}C and ^{13}C).

As in the case of carbon, the mass for each element listed in the table inside the front cover of the text is an average value based on the isotopic composition of the naturally occurring element. For instance, the mass listed for hydrogen (1.008) is the average mass for natural hydrogen, which is a mixture of ^1H and ^2H (deuterium). *No* atom of hydrogen actually has the mass 1.008.

CHEMICAL IMPACT

Buckyballs Teach Some History

About 250 million years ago, 90% of life on earth was destroyed in some sort of cataclysmic event. This event, which ended the Permian period and began the Triassic (the P-T boundary), is the most devastating mass extinction in the earth's history—far surpassing the catastrophe 65 million years ago that wiped out the dinosaurs (the K-T boundary). In 1979 geologist Walter Alvarez and his Nobel Prize-winning physicist father Luis Alvarez suggested that unusually high concentrations of iridium in rocks laid down at the K-T boundary meant that an asteroid had hit the earth, causing tremendous devastation. In the last 20 years much evidence has accumulated to support this hypothesis, including identification of the location of the probable crater caused by the impact in the ocean near Mexico.

Were the P-T boundary extinctions also caused by an extraterrestrial object or by some event on earth, such as a massive volcano explosion? Recent discoveries by geo-

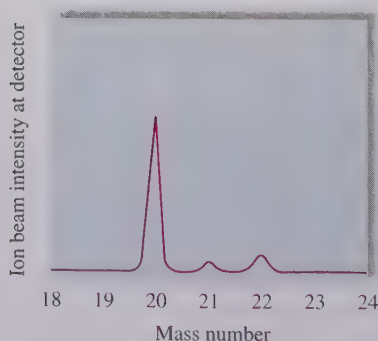
chemists Luann Becker of the University of Washington and Robert J. Poreda of the University of Rochester seem to strongly support the impact theory. Examining sediment from China and Japan, the team found fullerenes encapsulating argon and helium gas atoms whose isotopic composition indicates that they are extraterrestrial in origin. For example, the ratio of ^3He to ^4He found in the fullerenes is 100 times greater than the ratio for helium found in the earth's atmosphere. Likewise, the isotopic composition of the fullerene-trapped argon atoms is quite different from that found on earth.

Recall that fullerenes include spherical C_{60} carbon molecules ("buckyballs") whose cavities can trap other atoms such as helium and argon. (See the accompanying figure.) The scientists postulate that the fullerenes originated in stars or collapsing gas clouds where the noble gas atoms were trapped as the fullerenes formed. These

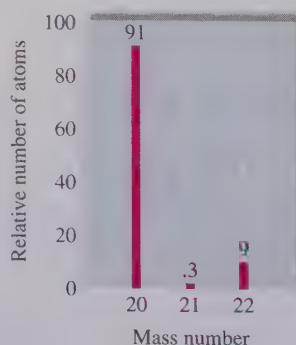
In addition to being useful for determining accurate mass values for individual atoms, the mass spectrometer is used to determine the isotopic composition of a natural element. For example, when a sample of natural neon is injected into a mass spectrometer, the mass spectrum shown in Fig. 3.2 is obtained. The areas of the "peaks" or the heights of the bars indicate the relative abundances of $^{20}_{10}\text{Ne}$, $^{21}_{10}\text{Ne}$, and $^{22}_{10}\text{Ne}$ atoms.



(a)



(b)



(c)

FIGURE 3.2

(a) Neon gas glowing in a discharge tube. The relative intensities of the signals recorded when natural neon is injected into a mass spectrometer, represented in terms of (b) "peaks" and (c) a bar graph. The relative areas of the peaks are 0.9092 (^{20}Ne), 0.00257 (^{21}Ne), and 0.0882 (^{22}Ne); natural neon is therefore 90.92% ^{20}Ne , 0.257% ^{21}Ne , and 8.82% ^{22}Ne .

fullerenes were then somehow incorporated into the object that eventually hit the earth. Based on the isotopic compositions, the geochemists estimate that the impacting body must have been 10 kilometers in diameter, which is comparable in size to the asteroid that is assumed to have killed the dinosaurs.

One factor that had previously cast doubt on an asteroid collision as the cause of the P-T catastrophe was the lack of iridium found in sediments from this period. However, Becker and other scientists argue that this absence probably means the impacting object may have been a comet rather than an asteroid. It is also possible that such a blow could have intensified the volcanism already under way on earth at that time, delivering a “one-two punch” that almost obliterated life on earth, according to Becker.

It is ironic that “buckyballs,” which made big news when they were recently synthesized for the first time in the laboratory, actually have been around for millions of years and have some very interesting history to teach us.



Isotope ratios of the noble gas atoms inside celestial buckyballs indicate that these ancient carbon cages formed in a stellar environment, not on earth.

Figure from *Chemical and Engineering News*, Feb. 26, 2001, p. 9. Reprinted by permission of Joseph Wilmhoff.

SAMPLE EXERCISE 3.1



Copper nugget.

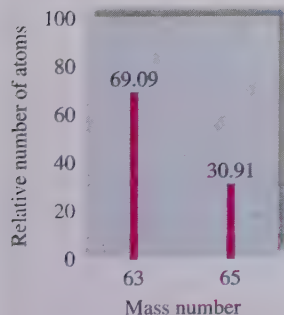


FIGURE 3.3
Mass spectrum of natural copper.

The Average Mass of an Element

When a sample of natural copper is vaporized and injected into a mass spectrometer, the results shown in Fig. 3.3 are obtained. Use these data to compute the average mass of natural copper. (The mass values for ^{63}Cu and ^{65}Cu are 62.93 amu and 64.93 amu, respectively.)

SOLUTION

As shown by the graph, of every 100 atoms of natural copper, 69.09 are ^{63}Cu and 30.91 are ^{65}Cu . Thus the mass of 100 atoms of natural copper is

$$(69.09 \text{ atoms}) \left(62.93 \frac{\text{amu}}{\text{atom}} \right) + (30.91 \text{ atoms}) \left(64.93 \frac{\text{amu}}{\text{atom}} \right) = 6355 \text{ amu}$$

The *average mass* of a copper atom is

$$\frac{6355 \text{ amu}}{100 \text{ atoms}} = 63.55 \text{ amu/atom}$$

This mass value is used in doing calculations involving the reactions of copper and is the value given in the table inside the front cover of this book.

See Exercises 3.21 and 3.22.

3.2 The Mole

The SI definition of the mole is the amount of a substance that contains as many entities as there are in exactly 12 g of carbon-12.

Avogadro's number is 6.022×10^{23} . One mole of anything is 6.022×10^{23} units of that substance.

Because samples of matter typically contain so many atoms, a unit of measure called the *mole* has been established for use in counting atoms. For our purposes, it is most convenient to define the **mole** (abbreviated mol) as *the number equal to the number of carbon atoms in exactly 12 grams of pure ^{12}C* . Techniques such as mass spectrometry, which count atoms very precisely, have been used to determine this number as 6.02214×10^{23} (6.022×10^{23} will be sufficient for our purposes). This number is called **Avogadro's number** to honor his contributions to chemistry. *One mole of something consists of 6.022×10^{23} units of that substance*. Just as a dozen eggs is 12 eggs, a mole of eggs is 6.022×10^{23} eggs.

The magnitude of the number 6.022×10^{23} is very difficult to imagine. To give you some idea, 1 mole of seconds represents a span of time 4 million times as long as the earth has already existed, and 1 mole of marbles is enough to cover the entire earth to a depth of 50 miles! However, since atoms are so tiny, a mole of atoms or molecules is a perfectly manageable quantity to use in a reaction (see Fig. 3.4).

How do we use the mole in chemical calculations? Recall that Avogadro's number is defined as the number of atoms in exactly 12 grams of ^{12}C . This means that 12 grams of ^{12}C contains 6.022×10^{23} atoms. It also means that a 12.01-gram sample of natural carbon contains 6.022×10^{23} atoms (a mixture of ^{12}C , ^{13}C , and ^{14}C atoms, with an average atomic mass of 12.01). Since the ratio of the masses of the samples (12 g/12.01 g) is the same as the ratio of the masses of the individual components (12 amu/12.01 amu), the two samples contain the *same number* of atoms (6.022×10^{23}).

To be sure this point is clear, think of oranges with an average mass of 0.5 pound each and grapefruit with an average mass of 1.0 pound each. Any two sacks for which the sack of grapefruit weighs twice as much as the sack of oranges will contain the same number of pieces of fruit. The same idea extends to atoms. Compare natural carbon (average mass of 12.01) and natural helium (average mass of 4.003). A sample of 12.01 grams of natural carbon contains the same number of atoms as



FIGURE 3.4

Proceeding clockwise from the top, samples containing one mole each of copper, aluminum, iron, sulfur, iodine, and (in the center) mercury.

TABLE 3.1 Comparison of 1 Mole Samples of Various Elements

Element	Number of Atoms Present	Mass of Sample (g)
Aluminum	6.022×10^{23}	26.98
Copper	6.022×10^{23}	63.55
Iron	6.022×10^{23}	55.85
Sulfur	6.022×10^{23}	32.07
Iodine	6.022×10^{23}	126.9
Mercury	6.022×10^{23}	200.6

4.003 grams of natural helium. Both samples contain 1 mole of atoms (6.022×10^{23}). Table 3.1 gives more examples that illustrate this basic idea.

Thus the mole is defined such that a sample of a natural element with a mass equal to the element's atomic mass expressed in grams contains 1 mole of atoms. This definition also fixes the relationship between the atomic mass unit and the gram. Since 6.022×10^{23} atoms of carbon (each with a mass of 12 amu) have a mass of 12 g, then

$$(6.022 \times 10^{23} \text{ atoms}) \left(\frac{12 \text{ amu}}{\text{atom}} \right) = 12 \text{ g}$$

and

$$6.022 \times 10^{23} \text{ amu} = 1 \text{ g}$$

$\uparrow$
 Exact
 number

This relationship can be used to derive the unit factor needed to convert between atomic mass units and grams.

SAMPLE EXERCISE 3.2

Determining the Mass of a Sample of Atoms

Americium is an element that does not occur naturally. It can be made in very small amounts in a device known as a *particle accelerator*. Compute the mass in grams of a sample of americium containing six atoms.

SOLUTION

From the table inside the front cover of the text, we note that one americium atom has a mass of 243 amu. Thus the mass of six atoms is

$$6 \text{ atoms} \times 243 \frac{\text{amu}}{\text{atom}} = 1.46 \times 10^3 \text{ amu}$$

Using the relationship

$$6.022 \times 10^{23} \text{ amu} = 1 \text{ g}$$

we write the conversion factor for converting atomic mass units to grams:

$$\frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}}$$

The mass of 1 mole of an element is equal to its atomic mass in grams.

CHEMICAL IMPACT

Elemental Analysis Catches Elephant Poachers

In an effort to combat the poaching of elephants by controlling illegal exports of ivory, scientists are now using the isotopic composition of ivory trinkets and elephant tusks to identify the region of Africa where the elephant lived. Using a mass spectrometer, scientists analyze the ivory for the relative amounts of ^{12}C , ^{13}C , ^{14}N , ^{15}N , ^{86}Sr , and ^{87}Sr to determine the diet of the elephant and thus its place of origin. For example, because grasses use a different photosynthetic pathway to produce glucose than do trees, grasses have a slightly different $^{13}\text{C}/^{12}\text{C}$ ratio from that of trees. They have different ratios because each time a carbon atom is added in going from simpler to more complex compounds, the more massive ^{13}C is disfavored relative to ^{12}C because it reacts more slowly. Because trees use more steps to build up glucose, they end up with a smaller $^{13}\text{C}/^{12}\text{C}$ ratio in their leaves relative to grasses, and this difference is then reflected in the tissues of elephants. Thus scientists can tell whether a

particular tusk came from a savanna-dwelling elephant (grass-eating) or from a tree-browsing elephant.

Similarly, because the ratios of $^{15}\text{N}/^{14}\text{N}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in elephant tusks also vary depending on the region of Africa the elephant inhabits, they can be used to trace the elephant's origin. In fact, using these techniques, scientists have reported being able to discriminate between elephants living only about 100 miles apart.

There is now international concern about the dwindling elephant populations in Africa—their numbers have decreased by 40% over the past decade. This concern has led to bans in the export of ivory from many countries in Africa. However, a few nations still allow ivory to be exported. Thus, to enforce the trade restrictions, the origin of a given piece of ivory must be established. It is hoped that the “isotope signature” of the ivory can be used for this purpose.

The mass of six americium atoms in grams is

$$1.46 \times 10^3 \text{ amu} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 2.42 \times 10^{-21} \text{ g}$$

See Exercise 3.27.

To do chemical calculations, you must understand what the mole means and how to determine the number of moles in a given mass of a substance. These procedures are illustrated in Sample Exercises 3.3 and 3.4.

SAMPLE EXERCISE 3.3

Determining Moles of Atoms

Aluminum (Al) is a metal with a high strength-to-mass ratio and a high resistance to corrosion; thus it is often used for structural purposes. Compute both the number of moles of atoms and the number of atoms in a 10.0-g sample of aluminum.

(left) Pure aluminum. (right) Aluminum alloys are used for many high-quality bicycle components, such as this chain wheel.



SOLUTION

The mass of 1 mole (6.022×10^{23} atoms) of aluminum is 26.98 g. The sample we are considering has a mass of 10.0 g. Since the mass is less than 26.98 g, this sample contains less than 1 mole of aluminum atoms. We can calculate the number of moles of aluminum atoms in 10.0 g as follows:

$$10.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 0.371 \text{ mol Al atoms}$$

The number of atoms in 10.0 g (0.371 mol) of aluminum is

$$0.371 \text{ mol Al} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Al}} = 2.23 \times 10^{23} \text{ atoms}$$

See Exercise 3.28.

SAMPLE EXERCISE 3.4**Calculating Numbers of Atoms**

A silicon chip used in an integrated circuit of a microcomputer has a mass of 5.68 mg. How many silicon (Si) atoms are present in the chip?

SOLUTION

The strategy for doing this problem is to convert from milligrams of silicon to grams of silicon, then to moles of silicon, and finally to atoms of silicon:

$$\begin{aligned} 5.68 \text{ mg Si} \times \frac{1 \text{ g Si}}{1000 \text{ mg Si}} &= 5.68 \times 10^{-3} \text{ g Si} \\ 5.68 \times 10^{-3} \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} &= 2.02 \times 10^{-4} \text{ mol Si} \\ 2.02 \times 10^{-4} \text{ mol Si} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Si}} &= 1.22 \times 10^{20} \text{ atoms} \end{aligned}$$

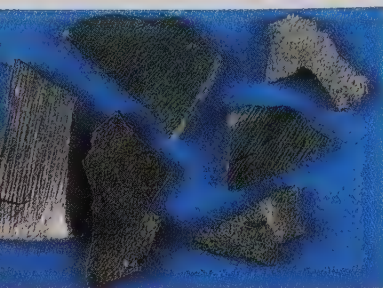
See Exercise 3.29.

Always check to see if your answer is sensible.

It always makes sense to think about whether your answer is reasonable as you do a calculation. In Sample Exercise 3.4, 5.68 mg of silicon is clearly much less than 1 mol of silicon (which has a mass of 28.09 g), so the final answer of 1.22×10^{20} atoms (compared with 6.022×10^{23} atoms) is at least in the right direction. Paying careful attention to units and making sure the answer is reasonable can help you detect an inverted conversion factor or a number that was incorrectly entered in your calculator.

SAMPLE EXERCISE 3.5**Calculating the Number of Moles and Mass**

Cobalt (Co) is a metal that is added to steel to improve its resistance to corrosion. Calculate both the number of moles in a sample of cobalt containing 5.00×10^{20} atoms and the mass of the sample.



Fragments of cobalt metal.

SOLUTION

Note that the sample of 5.00×10^{20} atoms of cobalt is less than 1 mole (6.022×10^{23} atoms) of cobalt. What fraction of a mole it represents can be determined as follows:

$$5.00 \times 10^{20} \text{ atoms Co} \times \frac{1 \text{ mol Co}}{6.022 \times 10^{23} \text{ atoms Co}} = 8.30 \times 10^{-4} \text{ mol Co}$$

Since the mass of 1 mole of cobalt atoms is 58.93 g, the mass of 5.00×10^{20} atoms can be determined as follows:

$$8.30 \times 10^{-4} \text{ mol Co} \times \frac{58.93 \text{ g Co}}{1 \text{ mol Co}} = 4.89 \times 10^{-2} \text{ g Co}$$

See Exercise 3.30.

3.3 Molar Mass

A chemical compound is, ultimately, a collection of atoms. For example, methane (the major component of natural gas) consists of molecules that each contain one carbon and four hydrogen atoms (CH_4). How can we calculate the mass of 1 mole of methane; that is, what is the mass of 6.022×10^{23} CH_4 molecules? Since each CH_4 molecule contains one carbon atom and four hydrogen atoms, 1 mole of CH_4 molecules contains 1 mole of carbon atoms and 4 moles of hydrogen atoms. The mass of 1 mole of methane can be found by summing the masses of carbon and hydrogen present:

$$\begin{array}{rcl} \text{Mass of 1 mol C} & = & 12.01 \text{ g} \\ \text{Mass of 4 mol H} & = & 4 \times 1.008 \text{ g} \\ \text{Mass of 1 mol CH}_4 & = & 16.04 \text{ g} \end{array}$$

Because 16.04 g represents the mass of 1 mole of methane molecules, it makes sense to call it the *molar mass* for methane. Thus the **molar mass** of a substance is *the mass in grams of one mole of the compound*. Traditionally, the term *molecular weight* has been used for this quantity. However, we will use molar mass exclusively in this text. The molar mass of a known substance is obtained by summing the masses of the component atoms as we did for methane.

Note that in this case, the term 12.01 limits the number of significant figures.

A substance's molar mass is the mass in grams of 1 mole of the substance.

SAMPLE EXERCISE 3.6

Calculating Molar Mass I

Juglone, a dye known for centuries, is produced from the husks of black walnuts. It is also a natural herbicide (weed killer) that kills off competitive plants around the black walnut tree but does not affect grass and other noncompetitive plants. The formula for juglone is $\text{C}_{10}\text{H}_6\text{O}_3$.

- Calculate the molar mass of juglone.
- A sample of 1.56×10^{-2} g of pure juglone was extracted from black walnut husks. How many moles of juglone does this sample represent?

CHEMICAL IMPACT

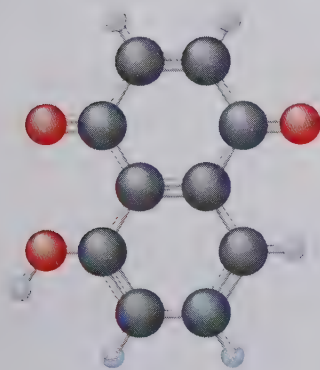
Measuring the Masses of Large Molecules, or Making Elephants Fly

When a chemist produces a new molecule, one crucial property for making a positive identification is the molecule's mass. There are many ways to determine the molar mass of a compound, but one of the fastest and most accurate methods involves mass spectrometry. This method requires that the substance be put into the gas phase and ionized. The deflection that the resulting ion exhibits as it is accelerated through a magnetic field can be used to obtain a very precise value of its mass. One drawback of this method is that it is difficult to use with large molecules because they are difficult to vaporize. That is, substances that contain large molecules typically have very high boiling points, and these molecules are often damaged when they are vaporized at such high temperatures. A case in point involves proteins, an extremely important class of large biologic molecules that are quite fragile at high temperatures. Typical methods used to obtain the masses of protein molecules are slow and tedious.

Mass spectrometry has not been used previously to obtain protein masses because proteins decompose at the

temperatures necessary to vaporize them. However, a new technique called *matrix-assisted laser desorption* has been developed that allows mass spectrometric determination of protein molar masses. In this technique, the large "target" molecule is embedded in a matrix of smaller molecules. The matrix is then placed in a mass spectrometer and blasted with a laser beam, which causes its disintegration. Disintegration of the matrix frees the large target molecule, which is then swept into the mass spectrometer. One researcher involved in this project likened this method to an elephant on top of a tall building: "The elephant must fly if the building is suddenly turned into fine grains of sand."

This technique allows scientists to determine the mass of huge molecules. So far researchers have measured proteins with masses up to 350,000 daltons (1 dalton is the mass of a hydrogen atom). This method, which makes mass spectrometry a routine tool for the determination of protein masses, probably will be extended to even larger molecules such as DNA and could be a revolutionary development in the characterization of biomolecules.



Juglone.

SOLUTION

- a. The molar mass is obtained by summing the masses of the component atoms. In 1 mole of juglone there are 10 moles of carbon atoms, 6 moles of hydrogen atoms, and 3 moles of oxygen atoms:

$$\begin{array}{rcl} 10 \text{ C:} & 10 \times 12.01 \text{ g} & = 120.1 \text{ g} \\ 6 \text{ H:} & 6 \times 1.008 \text{ g} & = 6.048 \text{ g} \\ 3 \text{ O:} & 3 \times 16.00 \text{ g} & = 48.00 \text{ g} \\ \text{Mass of 1 mol C}_{10}\text{H}_6\text{O}_3 & = & 174.1 \text{ g} \end{array}$$

The mass of 1 mole of juglone is 174.1 g, which is the molar mass.

- b. The mass of 1 mole of this compound is 174.1 g; thus $1.56 \times 10^{-2} \text{ g}$ is much less than a mole. The exact fraction of a mole can be determined as follows:

$$1.56 \times 10^{-2} \text{ g juglone} \times \frac{1 \text{ mol juglone}}{174.1 \text{ g juglone}} = 8.96 \times 10^{-5} \text{ mol juglone}$$

See Exercises 3.33 through 3.36.

SAMPLE EXERCISE 3.7

Calculating Molar Mass II

Calcium carbonate (CaCO_3), also called *calcite*, is the principal mineral found in limestone, marble, chalk, pearls, and the shells of marine animals such as clams.



Calcite crystals.

- a. Calculate the molar mass of calcium carbonate.
 b. A certain sample of calcium carbonate contains 4.86 moles. What is the mass in grams of this sample? What is the mass of the CO_3^{2-} ions present?

SOLUTION

- a. Calcium carbonate is an ionic compound composed of Ca^{2+} and CO_3^{2-} ions. In 1 mole of calcium carbonate there are 1 mole of Ca^{2+} ions and 1 mole of CO_3^{2-} ions. The molar mass is calculated by summing the masses of the components:

$$\begin{array}{rcl} 1 \text{ Ca}^{2+}: & 1 \times 40.08 \text{ g} = & 40.08 \text{ g} \\ 1 \text{ CO}_3^{2-}: & & \\ 1 \text{ C}: & 1 \times 12.01 \text{ g} = & 12.01 \text{ g} \\ 3 \text{ O}: & 3 \times 16.00 \text{ g} = & \underline{48.00 \text{ g}} \\ \text{Mass of 1 mol CaCO}_3 = & & 100.09 \text{ g} \end{array}$$

Thus the mass of 1 mole of CaCO_3 (1 mol Ca^{2+} plus 1 mol CO_3^{2-}) is 100.09 g. This is the molar mass.

- b. The mass of 1 mole of CaCO_3 is 100.09 g. The sample contains nearly 5 moles, or close to 500 g. The exact amount is determined as follows:

$$4.86 \text{ mol CaCO}_3 \times \frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 486 \text{ g CaCO}_3$$

To find the mass of carbonate ions (CO_3^{2-}) present in this sample, we must realize that 4.86 moles of CaCO_3 contains 4.86 moles of Ca^{2+} ions and 4.86 moles of CO_3^{2-} ions. The mass of 1 mole of CO_3^{2-} ions is

$$\begin{array}{rcl} 1 \text{ C}: & 1 \times 12.01 = & 12.01 \text{ g} \\ 3 \text{ O}: & 3 \times 16.00 = & \underline{48.00 \text{ g}} \\ \text{Mass of 1 mol CO}_3^{2-} = & & 60.01 \text{ g} \end{array}$$

Thus the mass of 4.86 moles of CO_3^{2-} ions is

$$4.86 \text{ mol CO}_3^{2-} \times \frac{60.01 \text{ g CO}_3^{2-}}{1 \text{ mol CO}_3^{2-}} = 292 \text{ g CO}_3^{2-}$$

See Exercises 3.37 through 3.40.

SAMPLE EXERCISE 3.8**Molar Mass and Numbers of Molecules**

Isopentyl acetate is the compound responsible for the scent of bananas. A molecular model of isopentyl acetate is shown in the margin on the next page. Interestingly, bees release about $1 \mu\text{g}$ ($1 \times 10^{-6} \text{ g}$) of this compound when they sting. The resulting scent attracts other bees to join the attack. How many molecules of isopentyl acetate are released in a typical bee sting? How many atoms of carbon are present?

Isopentyl acetate is released when a bee stings.

SOLUTION

Since we are given a mass of isopentyl acetate and want to find the number of molecules, we must first compute the molar mass:

$$7 \text{ mol C} \times 12.01 \frac{\text{g}}{\text{mol}} = 84.07 \text{ g C}$$

$$14 \text{ mol H} \times 1.008 \frac{\text{g}}{\text{mol}} = 14.11 \text{ g H}$$

$$2 \text{ mol O} \times 16.00 \frac{\text{g}}{\text{mol}} = \frac{32.00 \text{ g O}}{130.18 \text{ g}}$$

This means that 1 mole of isopentyl acetate (6.022×10^{23} molecules) has a mass of 130.18 g.

To find the number of molecules released in a sting, we must first determine the number of moles of isopentyl acetate in 1×10^{-6} g:

$$1 \times 10^{-6} \text{ g } \text{C}_7\text{H}_{14}\text{O}_2 \times \frac{1 \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2}{130.18 \text{ g } \text{C}_7\text{H}_{14}\text{O}_2} = 8 \times 10^{-9} \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2$$

Since 1 mole is 6.022×10^{23} units, we can determine the number of molecules:

$$8 \times 10^{-9} \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2 \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2} = 5 \times 10^{15} \text{ molecules}$$

To determine the number of carbon atoms present, we must multiply the number of molecules by 7, since each molecule of isopentyl acetate contains seven carbon atoms:

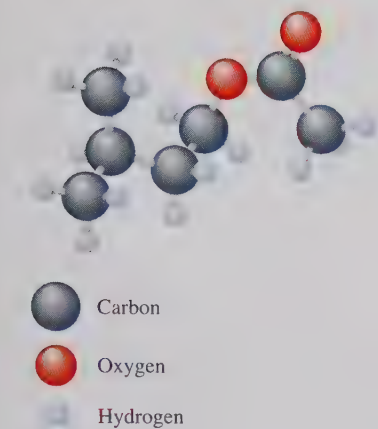
$$5 \times 10^{15} \text{ molecules} \times \frac{7 \text{ carbon atoms}}{\text{molecule}} = 4 \times 10^{16} \text{ carbon atoms}$$

NOTE:

In keeping with our practice of always showing the correct number of significant figures, we have rounded after each step. However, if extra digits are carried through this problem, the final answer rounds to 3×10^{16} .

See Exercises 3.41 through 3.46.

To show the correct number of significant figures in each calculation, we round after each step. In your calculations, always carry extra significant figures through to the end; then round.



Isopentyl acetate.

3.4 Percent Composition of Compounds

There are two common ways of describing the composition of a compound: in terms of the numbers of its constituent atoms and in terms of the percentages (by mass) of its elements. We can obtain the mass percents of the elements from the formula of the compound by comparing the mass of each element present in 1 mole of the compound to the total mass of 1 mole of the compound.

For example, for ethanol, which has the formula $\text{C}_2\text{H}_5\text{OH}$, the mass of each element present and the molar mass are obtained as follows:

$$\text{Mass of C} = 2 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 24.02 \text{ g}$$

$$\text{Mass of H} = 6 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 6.048 \text{ g}$$

$$\text{Mass of O} = 1 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 16.00 \text{ g}$$

$$\text{Mass of 1 mol } \text{C}_2\text{H}_5\text{OH} = 46.07 \text{ g}$$

The **mass percent** (often called the *weight percent*) of carbon in ethanol can be computed by comparing the mass of carbon in 1 mole of ethanol to the total mass of 1 mole of ethanol and multiplying the result by 100:

$$\begin{aligned}\text{Mass percent of C} &= \frac{\text{mass of C in 1 mol C}_2\text{H}_5\text{OH}}{\text{mass of 1 mol C}_2\text{H}_5\text{OH}} \times 100\% \\ &= \frac{24.02 \text{ g}}{46.07 \text{ g}} \times 100\% = 52.14\%\end{aligned}$$

The mass percents of hydrogen and oxygen in ethanol are obtained in a similar manner:

$$\begin{aligned}\text{Mass percent of H} &= \frac{\text{mass of H in 1 mol C}_2\text{H}_5\text{OH}}{\text{mass of 1 mol C}_2\text{H}_5\text{OH}} \times 100\% \\ &= \frac{6.048 \text{ g}}{46.07 \text{ g}} \times 100\% = 13.13\%\end{aligned}$$

$$\begin{aligned}\text{Mass percent of O} &= \frac{\text{mass of O in 1 mol C}_2\text{H}_5\text{OH}}{\text{mass of 1 mol C}_2\text{H}_5\text{OH}} \times 100\% \\ &= \frac{16.00 \text{ g}}{46.07 \text{ g}} \times 100\% = 34.73\%\end{aligned}$$

Notice that the percentages add up to 100.00%; this provides a check that the calculations are correct.

SAMPLE EXERCISE 3.9

Calculating Mass Percent I

Carvone is a substance that occurs in two forms having different arrangements of the atoms but the same molecular formula ($\text{C}_{10}\text{H}_{14}\text{O}$) and mass. One type of carvone gives caraway seeds their characteristic smell, and the other type is responsible for the smell of spearmint oil. Compute the mass percent of each element in carvone.

SOLUTION

The masses of the elements in 1 mole of carvone are

$$\text{Mass of C in 1 mol} = 10 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 120.1 \text{ g}$$

$$\text{Mass of H in 1 mol} = 14 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 14.11 \text{ g}$$

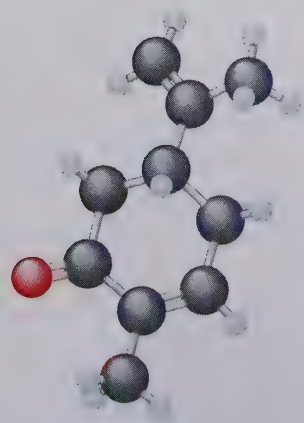
$$\text{Mass of O in 1 mol} = 1 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 16.00 \text{ g}$$

$$\text{Mass of 1 mol C}_{10}\text{H}_{14}\text{O} = 150.2 \text{ g}$$

Next we find the fraction of the total mass contributed by each element and convert it to a percentage:

$$\text{Mass percent of C} = \frac{120.1 \text{ g C}}{150.2 \text{ g C}_{10}\text{H}_{14}\text{O}} \times 100\% = 79.96\%$$

$$\text{Mass percent of H} = \frac{14.11 \text{ g H}}{150.2 \text{ g C}_{10}\text{H}_{14}\text{O}} \times 100\% = 9.394\%$$



Carvone.

$$\text{Mass percent of O} = \frac{16.00 \text{ g O}}{150.2 \text{ g C}_{10}\text{H}_{14}\text{O}} \times 100\% = 10.65\%$$

CHECK:

Sum the individual mass percent values—they should total to 100% within round-off errors. In this case, the percentages add up to 100.00%.

See Exercises 3.53 and 3.54.

SAMPLE EXERCISE 3.10

Although Fleming is commonly given credit for the discovery of penicillin, there is good evidence that penicillium mold extracts were used in the nineteenth century by Lord Joseph Lister to cure infections.

Calculating Mass Percent II

Penicillin, the first of a now large number of antibiotics (antibacterial agents), was discovered accidentally by the Scottish bacteriologist Alexander Fleming in 1928, but he was never able to isolate it as a pure compound. This and similar antibiotics have saved millions of lives that might have been lost to infections. Penicillin F has the formula $\text{C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4$. Compute the mass percent of each element.

SOLUTION

The molar mass of penicillin F is computed as follows:

$$\text{C: } 14 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 168.1 \text{ g}$$

$$\text{H: } 20 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 20.16 \text{ g}$$

$$\text{N: } 2 \text{ mol} \times 14.01 \frac{\text{g}}{\text{mol}} = 28.02 \text{ g}$$

$$\text{S: } 1 \text{ mol} \times 32.07 \frac{\text{g}}{\text{mol}} = 32.07 \text{ g}$$

$$\text{O: } 4 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 64.00 \text{ g}$$

$$\text{Mass of 1 mol C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4 = 312.4 \text{ g}$$

$$\text{Mass percent of C} = \frac{168.1 \text{ g C}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 53.81\%$$

$$\text{Mass percent of H} = \frac{20.16 \text{ g H}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 6.453\%$$

$$\text{Mass percent of N} = \frac{28.02 \text{ g N}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 8.969\%$$

$$\text{Mass percent of S} = \frac{32.07 \text{ g S}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 10.27\%$$

$$\text{Mass percent of O} = \frac{64.00 \text{ g O}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 20.49\%$$

CHECK:

The percentages add up to 99.99%.

See Exercises 3.55 and 3.56.



Penicillin is isolated from a mold that can be grown in large quantities in fermentation tanks.

3.5 Determining the Formula of a Compound

When a new compound is prepared, one of the first items of interest is the formula of the compound. This is most often determined by taking a weighed sample of the compound and either decomposing it into its component elements or reacting it with oxygen to produce substances such as CO_2 , H_2O , and N_2 , which are then collected and weighed. A device for doing this type of analysis is shown in Fig. 3.5. The results of such analyses provide the mass of each type of element in the compound, which can be used to determine the mass percent of each element.

We will see how information of this type can be used to compute the formula of a compound. Suppose a substance has been prepared that is composed of carbon, hydrogen, and nitrogen. When 0.1156 gram of this compound is reacted with oxygen, 0.1638 gram of carbon dioxide (CO_2) and 0.1676 gram of water (H_2O) are collected. Assuming that all the carbon in the compound is converted to CO_2 , we can determine the mass of carbon originally present in the 0.1156-gram sample. To do this, we must use the fraction (by mass) of carbon in CO_2 . The molar mass of CO_2 is

$$\text{C: } 1 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 12.01 \text{ g}$$

$$\text{O: } 2 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 32.00 \text{ g}$$

$$\text{Molar mass of } \text{CO}_2 = 44.01 \text{ g/mol}$$

The fraction of carbon present by mass is

$$\frac{\text{Mass of C}}{\text{Total mass of } \text{CO}_2} = \frac{12.01 \text{ g C}}{44.01 \text{ g } \text{CO}_2}$$

This factor can now be used to determine the mass of carbon in 0.1638 gram of CO_2 :

$$0.1638 \text{ g } \text{CO}_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g } \text{CO}_2} = 0.04470 \text{ g C}$$



CO_2 .



H_2O .

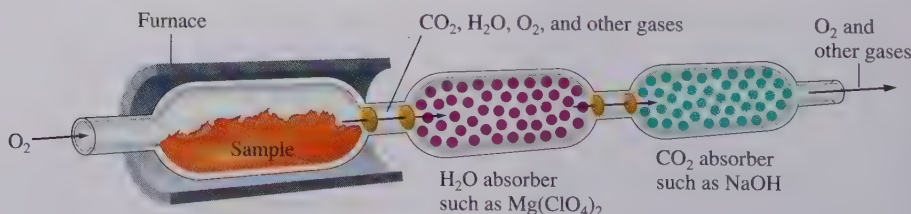


FIGURE 3.5

A schematic diagram of the combustion device used to analyze substances for carbon and hydrogen. The sample is burned in the presence of excess oxygen, which converts all its carbon to carbon dioxide and all its hydrogen to water. These products are collected by absorption using appropriate materials, and their amounts are determined by measuring the increase in masses of the absorbents.

Remember that this carbon originally came from the 0.1156-gram sample of unknown compound. Thus the mass percent of carbon in this compound is

$$\frac{0.04470 \text{ g C}}{0.1156 \text{ g compound}} \times 100\% = 38.67\% \text{ C}$$

The same procedure can be used to find the mass percent of hydrogen in the unknown compound. We assume that all the hydrogen present in the original 0.1156 gram of compound was converted to H_2O . The molar mass of H_2O is 18.02 grams, and the fraction of hydrogen by mass in H_2O is

$$\frac{\text{Mass of H}}{\text{Mass of H}_2\text{O}} = \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}}$$

Therefore, the mass of hydrogen in 0.1676 gram of H_2O is

$$0.1676 \text{ g } \text{H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.02 \text{ g } \text{H}_2\text{O}} = 0.01875 \text{ g H}$$

The mass percent of hydrogen in the compound is

$$\frac{0.01875 \text{ g H}}{0.1156 \text{ g compound}} \times 100\% = 16.22\% \text{ H}$$

The unknown compound contains only carbon, hydrogen, and nitrogen. So far we have determined that it is 38.67% carbon and 16.22% hydrogen. The remainder must be nitrogen:

$$100.00\% - (38.67\% + 16.22\%) = 45.11\% \text{ N}$$

$\begin{array}{ccc} \uparrow & & \uparrow \\ \% \text{ C} & & \% \text{ H} \end{array}$

We have determined that the compound contains 38.67% carbon, 16.22% hydrogen, and 45.11% nitrogen. Next we use these data to obtain the formula.

Since the formula of a compound indicates the *numbers* of atoms in the compound, we must convert the masses of the elements to numbers of atoms. The easiest way to do this is to work with 100.00 grams of the compound. In the present case, 38.67% carbon by mass means 38.67 grams of carbon per 100.00 grams of compound; 16.22% hydrogen means 16.22 grams of hydrogen per 100.00 grams of compound; and so on. To determine the formula, we must calculate the number of carbon atoms in 38.67 grams of carbon, the number of hydrogen atoms in 16.22 grams of hydrogen, and the number of nitrogen atoms in 45.11 grams of nitrogen. We can do this as follows:

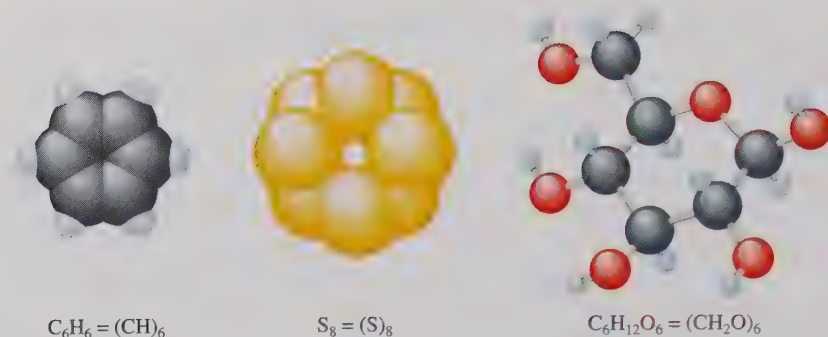
$$38.67 \text{ g } \text{C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.220 \text{ mol C}$$

$$16.22 \text{ g } \text{H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 16.09 \text{ mol H}$$

$$45.11 \text{ g } \text{N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 3.219 \text{ mol N}$$

Thus 100.00 grams of this compound contains 3.220 moles of carbon atoms, 16.09 moles of hydrogen atoms, and 3.219 moles of nitrogen atoms.

We can find the smallest *whole-number ratio* of atoms in this compound by dividing each of the mole values above by the smallest of the three:

**FIGURE 3.6**

Examples of substances whose empirical and molecular formulas differ. Notice that molecular formula = (empirical formula) $_n$, where n is an integer.

$$\begin{aligned}\text{C: } \frac{3.220}{3.220} &= 1.000 = 1 \\ \text{H: } \frac{16.09}{3.220} &= 4.997 = 5 \\ \text{N: } \frac{3.219}{3.220} &= 1.000 = 1\end{aligned}$$

Thus the formula might well be CH_5N . However, it also could be $\text{C}_2\text{H}_{10}\text{N}_2$ or $\text{C}_3\text{H}_{15}\text{N}_3$, and so on—that is, some multiple of the smallest whole-number ratio. Each of these alternatives also has the correct relative numbers of atoms. That is, any molecule that can be represented as $(\text{CH}_5\text{N})_n$, where n is an integer, has the **empirical formula** CH_5N . To be able to specify the exact formula of the molecule involved, the **molecular formula**, we must know the molar mass.

Suppose we know that this compound with empirical formula CH_5N has a molar mass of 31.06 g/mol. How do we determine which of the possible choices represents the molecular formula? Since the molecular formula is always a whole-number multiple of the empirical formula, we must first find the empirical formula mass for CH_5N :

$$\begin{aligned}1 \text{ C: } 1 \times 12.01 \text{ g} &= 12.01 \text{ g} \\ 5 \text{ H: } 5 \times 1.008 \text{ g} &= 5.040 \text{ g} \\ 1 \text{ N: } 1 \times 14.01 \text{ g} &= 14.01 \text{ g} \\ \text{Formula mass of } \text{CH}_5\text{N} &= 31.06 \text{ g/mol}\end{aligned}$$

This is the same as the known molar mass of the compound. Thus in this case the empirical formula and the molecular formula are the same; this substance consists of molecules with the formula CH_5N . It is quite common for the empirical and molecular formulas to be different; some examples where this is the case are shown in Fig. 3.6.

SAMPLE EXERCISE 3.11

Determining Empirical and Molecular Formulas I

Determine the empirical and molecular formulas for a compound that gives the following percentages upon analysis (in mass percents):

$$71.65\% \text{ Cl} \qquad 24.27\% \text{ C} \qquad 4.07\% \text{ H}$$

The molar mass is known to be 98.96 g/mol.

Molecular formula = (empirical formula) $_n$,
where n is an integer.

SOLUTION

First, we convert the mass percents to masses in grams. In 100.00 g of this compound there are 71.65 g of chlorine, 24.27 g of carbon, and 4.07 g of hydrogen. We use these masses to compute the moles of atoms present:

$$71.65 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 2.021 \text{ mol Cl}$$

$$24.27 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.021 \text{ mol C}$$

$$4.07 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.04 \text{ mol H}$$

Dividing each mole value by 2.021 (the smallest number of moles present), we obtain the empirical formula ClCH_2 .

To determine the molecular formula, we must compare the empirical formula mass with the molar mass. The empirical formula mass is 49.48 g/mol (confirm this). The molar mass is known to be 98.96 g/mol.

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96 \text{ g/mol}}{49.48 \text{ g/mol}} = 2$$

$$\text{Molecular formula} = (\text{ClCH}_2)_2 = \text{Cl}_2\text{C}_2\text{H}_4$$

This substance is composed of molecules with the formula $\text{Cl}_2\text{C}_2\text{H}_4$.

Notice that the method we employ here allows us to determine the molecular formula of a compound but not its structural formula. The compound $\text{Cl}_2\text{C}_2\text{H}_4$ is called *dichloroethane*. There are two forms of this compound, shown in Fig. 3.7. The form on the right was formerly used as an additive in leaded gasoline.

See Exercises 3.67 and 3.68.



FIGURE 3.7
The two forms of dichloroethane.

SAMPLE EXERCISE 3.12

Determining Empirical and Molecular Formulas II

A white powder is analyzed and found to contain 43.64% phosphorus and 56.36% oxygen by mass. The compound has a molar mass of 283.88 g/mol. What are the compound's empirical and molecular formulas?

SOLUTION

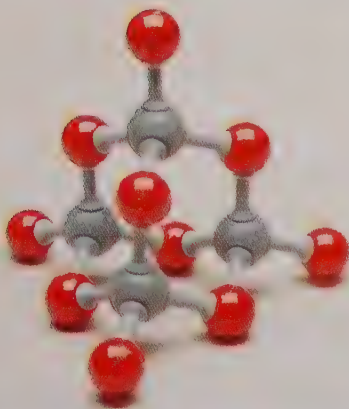
In 100.00 g of this compound there are 43.64 g of phosphorus and 56.36 g of oxygen. In terms of moles, in 100.00 g of the compound we have

$$43.64 \text{ g P} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} = 1.409 \text{ mol P}$$

$$56.36 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.523 \text{ mol O}$$

Dividing both mole values by the smaller one gives

$$\frac{1.409}{1.409} = 1 \text{ P} \quad \text{and} \quad \frac{3.523}{1.409} = 2.5 \text{ O}$$

**FIGURE 3.8**

The structure of P_4O_{10} . Note that some of the oxygen atoms act as “bridges” between the phosphorus atoms. This compound has a great affinity for water and is often used as a desiccant, or drying agent.

This yields the formula $PO_{2.5}$. Since compounds must contain whole numbers of atoms, the empirical formula should contain only whole numbers. To obtain the simplest set of whole numbers, we multiply both numbers by 2 to give the empirical formula P_2O_5 .

To obtain the molecular formula, we must compare the empirical formula mass to the molar mass. The empirical formula mass for P_2O_5 is 141.94.

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{283.88}{141.94} = 2$$

The molecular formula is $(P_2O_5)_2$, or P_4O_{10} .

The structural formula of this interesting compound is given in Fig. 3.8.

See Exercises 3.69 and 3.70.

In Sample Exercises 3.11 and 3.12 we found the molecular formula by comparing the empirical formula mass with the molar mass. There is an alternate way to obtain the molecular formula. For example, in Sample Exercise 3.11 we know the molar mass of the compound is 98.96 g/mol. This means that 1 mole of the compound weighs 98.96 grams. Since we also know the mass percentages of each element, we can compute the mass of each element present in 1 mole of compound:

$$\begin{aligned} \text{Chlorine: } & \frac{71.65 \text{ g Cl}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{70.90 \text{ g Cl}}{\text{mol compound}} \\ \text{Carbon: } & \frac{24.27 \text{ g C}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{24.02 \text{ g C}}{\text{mol compound}} \\ \text{Hydrogen: } & \frac{4.07 \text{ g H}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{4.03 \text{ g H}}{\text{mol compound}} \end{aligned}$$

Now we can compute moles of atoms present per mole of compound:

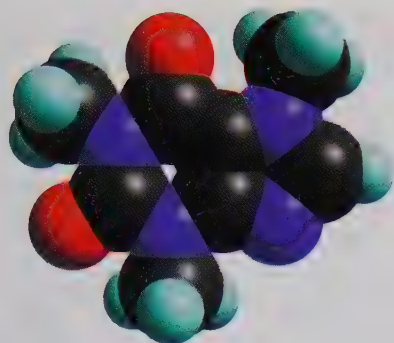
$$\begin{aligned} \text{Chlorine: } & \frac{70.90 \text{ g Cl}}{\text{mol compound}} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = \frac{2.000 \text{ mol Cl}}{\text{mol compound}} \\ \text{Carbon: } & \frac{24.02 \text{ g C}}{\text{mol compound}} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = \frac{2.000 \text{ mol C}}{\text{mol compound}} \\ \text{Hydrogen: } & \frac{4.03 \text{ g H}}{\text{mol compound}} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = \frac{4.00 \text{ mol H}}{\text{mol compound}} \end{aligned}$$

Thus 1 mole of the compound contains 2 mol Cl atoms, 2 mol C atoms, and 4 mol H atoms, and the molecular formula is $Cl_2C_2H_4$, as obtained in Sample Exercise 3.11.

SAMPLE EXERCISE 3.13

Determining a Molecular Formula

Caffeine, a stimulant found in coffee, tea, and chocolate, contains 49.48% carbon, 5.15% hydrogen, 28.87% nitrogen, and 16.49% oxygen by mass and has a molar mass of 194.2 g/mol. Determine the molecular formula of caffeine.



Computer-generated molecule of caffeine.

SOLUTION

We will first determine the mass of each element in 1 mole (194.2 g) of caffeine:

$$\begin{array}{l}
 \frac{49.48 \text{ g C}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{96.09 \text{ g C}}{\text{mol caffeine}} \\
 \frac{5.15 \text{ g H}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{10.0 \text{ g H}}{\text{mol caffeine}} \\
 \frac{28.87 \text{ g N}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{56.07 \text{ g N}}{\text{mol caffeine}} \\
 \frac{16.49 \text{ g O}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{32.02 \text{ g O}}{\text{mol caffeine}}
 \end{array}$$

Now we will convert to moles:

$$\begin{array}{l}
 \text{Carbon: } \frac{96.09 \text{ g}\cancel{\text{C}}}{\text{mol caffeine}} \times \frac{1 \text{ mol C}}{12.01 \text{ g}\cancel{\text{C}}} = \frac{8.001 \text{ mol C}}{\text{mol caffeine}} \\
 \text{Hydrogen: } \frac{10.0 \text{ g}\cancel{\text{H}}}{\text{mol caffeine}} \times \frac{1 \text{ mol H}}{1.008 \text{ g}\cancel{\text{H}}} = \frac{9.92 \text{ mol H}}{\text{mol caffeine}} \\
 \text{Nitrogen: } \frac{56.07 \text{ g}\cancel{\text{N}}}{\text{mol caffeine}} \times \frac{1 \text{ mol N}}{14.01 \text{ g}\cancel{\text{N}}} = \frac{4.002 \text{ mol N}}{\text{mol caffeine}} \\
 \text{Oxygen: } \frac{32.02 \text{ g}\cancel{\text{O}}}{\text{mol caffeine}} \times \frac{1 \text{ mol O}}{16.00 \text{ g}\cancel{\text{O}}} = \frac{2.001 \text{ mol O}}{\text{mol caffeine}}
 \end{array}$$

Rounding the numbers to integers gives the molecular formula for caffeine: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$.

See Exercises 3.69 and 3.70.

The methods for obtaining empirical and molecular formulas are summarized as follows:

Empirical Formula Determination

- Since mass percentage gives the number of grams of a particular element per 100 grams of compound, base the calculation on 100 grams of compound. Each percent will then represent the mass in grams of that element.
- Determine the number of moles of each element present in 100 grams of compound using the atomic masses of the elements present.
- Divide each value of the number of moles by the smallest of the values. If each resulting number is a whole number (after appropriate rounding), these numbers represent the subscripts of the elements in the empirical formula.
- If the numbers obtained in the previous step are not whole numbers, multiply each number by an integer so that the results are all whole numbers.

Numbers very close to whole numbers, such as 9.92 and 1.08, should be rounded to whole numbers. Numbers such as 2.25, 4.33, and 2.72 should not be rounded to whole numbers.

Molecular Formula Determination

Method One

- Obtain the empirical formula.
- Compute the mass corresponding to the empirical formula.
- Calculate the ratio

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

- The integer from the previous step represents the number of empirical formula units in one molecule. When the empirical formula subscripts are multiplied by this integer, the molecular formula results. This procedure is summarized by the equation:

$$\text{Molecular formula} = (\text{empirical formula}) \times \frac{\text{molar mass}}{\text{empirical formula mass}}$$

Method Two

- Using the mass percentages and the molar mass, determine the mass of each element present in one mole of compound.
- Determine the number of moles of each element present in one mole of compound.
- The integers from the previous step represent the subscripts in the molecular formula.

Note that method two assumes that the molar mass of the compound is known accurately.

3.6 Chemical Equations

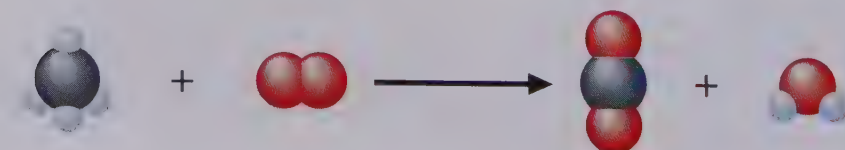
Chemical Reactions

A chemical change involves a reorganization of the atoms in one or more substances. For example, when the methane (CH_4) in natural gas combines with oxygen (O_2) in the air and burns, carbon dioxide (CO_2) and water (H_2O) are formed. This process is represented by a **chemical equation** with the **reactants** (here methane and oxygen) on the left side of an arrow and the **products** (carbon dioxide and water) on the right side:



Notice that the atoms have been reorganized. *Bonds have been broken, and new ones have been formed.* It is important to recognize that *in a chemical reaction, atoms are neither created nor destroyed. All atoms present in the reactants must be accounted for among the products.* In other words, there must be the same number of each type of atom on the product side and on the reactant side of the arrow. Making sure that this rule is obeyed is called **balancing a chemical equation** for a reaction.

The equation (shown above) for the reaction between CH_4 and O_2 is not balanced. We can see this from the following representation of the reaction:





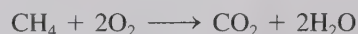
Methane reacts with oxygen to produce the flame in a Bunsen burner.

Notice that the number of oxygen atoms (in O_2) on the left of the arrow is two, while on the right there are three O atoms (in CO_2 and H_2O). Also, there are four hydrogen atoms (in CH_4) on the left and only two (in H_2O) on the right. Remember that a chemical reaction is simply a rearrangement of the atoms (a change in the way they are organized). Atoms are not created or destroyed in a chemical reaction. Thus the reactants and products must occur in numbers that give the same number of each type of atom among both the reactants and products. Simple trial and error will allow us to figure this out for the reaction of methane with oxygen. The needed numbers of molecules are

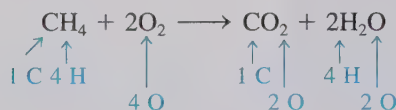


Notice that now we have the same number of each type of atom represented among the reactants and the products.

We can represent the preceding situation in a shorthand manner by the following chemical equation:



We can check that the equation is balanced by comparing the number of each type of atom on both sides:



To summarize, we have

Reactants	Products
1 C	1 C
4 H	4 H
4 O	4 O

The Meaning of a Chemical Equation

The chemical equation for a reaction gives two important types of information: the nature of the reactants and products and the relative numbers of each.

The reactants and products in a specific reaction must be identified by experiment. Besides specifying the compounds involved in the reaction, the equation often gives the *physical states* of the reactants and products:



Visualization: Oxygen, Hydrogen, Soap Bubbles, and Balloons

State	Symbol
Solid	(s)
Liquid	(l)
Gas	(g)
Dissolved in water (in aqueous solution)	(aq)

TABLE 3.2 Information Conveyed by the Balanced Equation for the Combustion of Methane

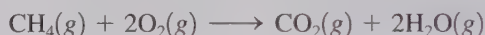
Reactants		Products
$\text{CH}_4(g) + 2\text{O}_2(g)$	$\longrightarrow$	$\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
1 molecule + 2 molecules	$\longrightarrow$	1 molecule + 2 molecules
1 mole + 2 moles	$\longrightarrow$	1 mole + 2 moles
6.022×10^{23} molecules + 2 (6.022×10^{23} molecules)	$\longrightarrow$	6.022×10^{23} molecules + 2 (6.022×10^{23} molecules)
16 g + 2 (32 g)	$\longrightarrow$	44 g + 2 (18 g)
80 g reactants	$\longrightarrow$	80 g products



For example, when hydrochloric acid in aqueous solution is added to solid sodium hydrogen carbonate, the products carbon dioxide gas, liquid water, and sodium chloride (which dissolves in the water) are formed:



The relative numbers of reactants and products in a reaction are indicated by the *coefficients* in the balanced equation. (The coefficients can be determined because we know that the same number of each type of atom must occur on both sides of the equation.) For example, the balanced equation



can be interpreted in several equivalent ways, as shown in Table 3.2. Note that the total mass is 80 grams for both reactants and products. We expect the mass to remain constant, since chemical reactions involve only a rearrangement of atoms. Atoms, and therefore mass, are conserved in a chemical reaction.

From this discussion you can see that a balanced chemical equation gives you a great deal of information.

3.7 Balancing Chemical Equations

An unbalanced chemical equation is of limited use. Whenever you see an equation, you should ask yourself whether it is balanced. The principle that lies at the heart of the balancing process is that atoms are conserved in a chemical reaction. The same number of each type of atom must be found among the reactants and products. It is also important to recognize that the identities of the reactants and products of a reaction are determined by experimental observation. For example, when liquid ethanol is burned in the presence of sufficient oxygen gas, the products are always carbon dioxide and water. When the equation for this reaction is balanced, the *identities* of the reactants and products must not be changed. *The formulas of the compounds must never be changed in balancing a chemical equation.* That is, the subscripts in a formula cannot be changed, nor can atoms be added or subtracted from a formula.

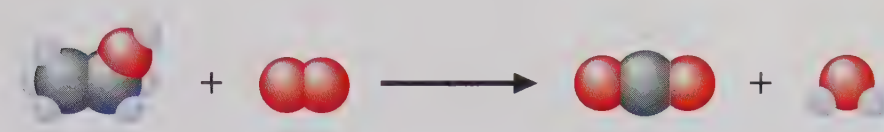
Most chemical equations can be balanced by inspection, that is, by trial and error. It is always best to start with the most complicated molecules (those containing the greatest number of atoms). For example, consider the reaction of ethanol with oxygen, given by the unbalanced equation

Understanding Concepts:
Conservation of Mass and
Balancing Equations

In balancing equations, start with the most complicated molecule.

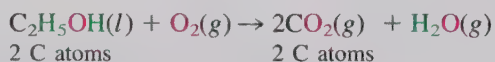


which can be represented by the following molecular models:

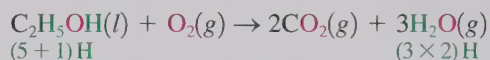


Notice that the carbon and hydrogen atoms are not balanced. There are two carbon atoms on the left and one on the right, and there are six hydrogens on the left and two on the right. We need to find the correct numbers of reactants and products so that we have the same number of all types of atoms among the reactants and products. We will balance the equation “by inspection” (a systematic trial-and-error procedure).

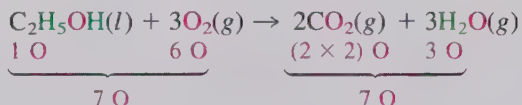
The most complicated molecule here is C₂H₅OH. We will begin by balancing the products that contain the atoms in C₂H₅OH. Since C₂H₅OH contains two carbon atoms, we place the coefficient 2 before the CO₂ to balance the carbon atoms:



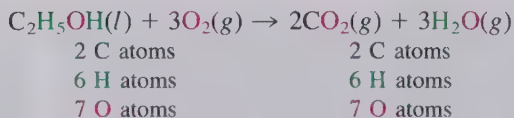
Since C₂H₅OH contains six hydrogen atoms, the hydrogen atoms can be balanced by placing a 3 before the H₂O:



Last, we balance the oxygen atoms. Note that the right side of the preceding equation contains seven oxygen atoms, whereas the left side has only three. We can correct this by putting a 3 before the O₂ to produce the balanced equation:

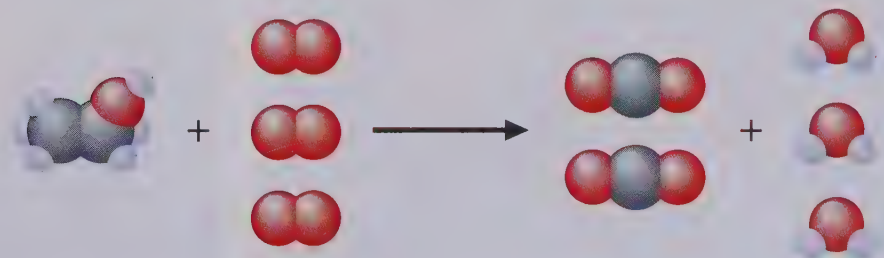


Now we check:



The equation is balanced.

The balanced equation can be represented as follows:



You can see that all the elements balance.

Writing and Balancing the Equation for a Chemical Reaction

- ➡ **1** Determine what reaction is occurring. What are the reactants, the products, and the physical states involved?
- ➡ **2** Write the *unbalanced* equation that summarizes the reaction described in step 1.
- ➡ **3** Balance the equation by inspection, starting with the most complicated molecule(s). Determine what coefficients are necessary so that the same number of each type of atom appears on both reactant and product sides. Do not change the identities (formulas) of any of the reactants or products.

SAMPLE EXERCISE 3.14

Chromate and dichromate compounds are carcinogens (cancer-inducing agents) and should be handled very carefully.

Balancing a Chemical Equation I

Chromium compounds exhibit a variety of bright colors. When solid ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, a vivid orange compound, is ignited, a spectacular reaction occurs, as shown in the two photographs below. Although the reaction is actually somewhat more complex, let's assume here that the products are solid chromium(III) oxide, nitrogen gas (consisting of N_2 molecules), and water vapor. Balance the equation for this reaction.

SOLUTION

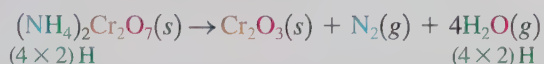
STEP 1 From the description given, the reactant is solid ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s)$, and the products are nitrogen gas, $\text{N}_2(g)$, water vapor, $\text{H}_2\text{O}(g)$, and solid chromium(III) oxide, $\text{Cr}_2\text{O}_3(s)$. The formula for chromium(III) oxide can be determined by recognizing that the Roman numeral III means that Cr^{3+} ions are present. For a neutral compound, the formula must then be Cr_2O_3 , since each oxide ion is O^{2-} .

STEP 2 The unbalanced equation is



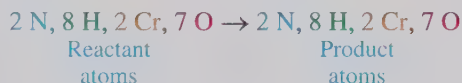
Decomposition of ammonium dichromate.

STEP 3 Note that nitrogen and chromium are balanced (two nitrogen atoms and two chromium atoms on each side), but hydrogen and oxygen are not. A coefficient of 4 for H_2O balances the hydrogen atoms:



Note that in balancing the hydrogen we also have balanced the oxygen, since there are seven oxygen atoms in the reactants and in the products.

CHECK:



The equation is balanced.

See Exercises 3.75 and 3.76.

SAMPLE EXERCISE 3.15

The Ostwald process is described in Section 20.2.

Balancing a Chemical Equation II

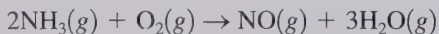
At 1000°C , ammonia gas, $\text{NH}_3(g)$, reacts with oxygen gas to form gaseous nitric oxide, $\text{NO}(g)$, and water vapor. This reaction is the first step in the commercial production of nitric acid by the Ostwald process. Balance the equation for this reaction.

SOLUTION

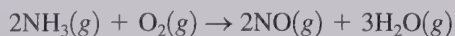
The unbalanced equation for the reaction is



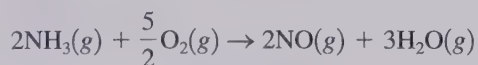
Because all the molecules in this equation are of about equal complexity, where we start in balancing it is rather arbitrary. Let's begin by balancing the hydrogen. A coefficient of 2 for NH_3 and a coefficient of 3 for H_2O give six atoms of hydrogen on both sides:



The nitrogen can be balanced with a coefficient of 2 for NO :



Finally, note that there are two atoms of oxygen on the left and five on the right. The oxygen can be balanced with a coefficient of $\frac{5}{2}$ for O_2 :



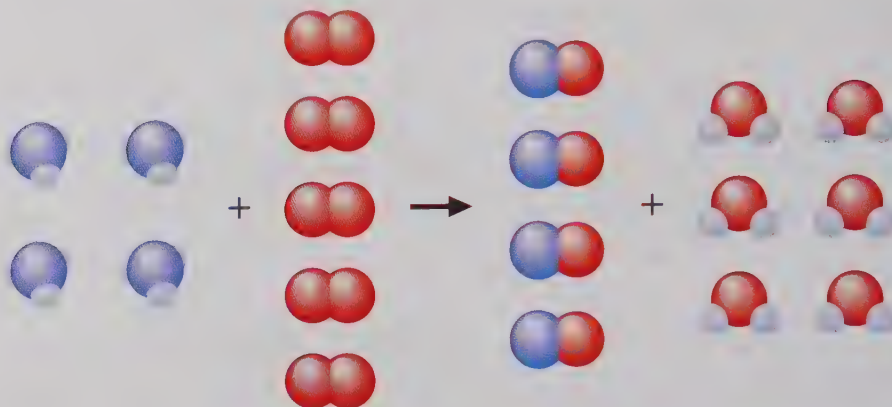
However, the usual custom is to have whole-number coefficients. We simply multiply the entire equation by 2.



CHECK:

There are 4 N, 12 H, and 10 O on both sides, so the equation is balanced.

We can represent this balanced equation visually as

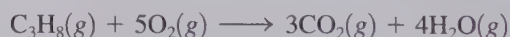


See Exercises 3.77 through 3.84.

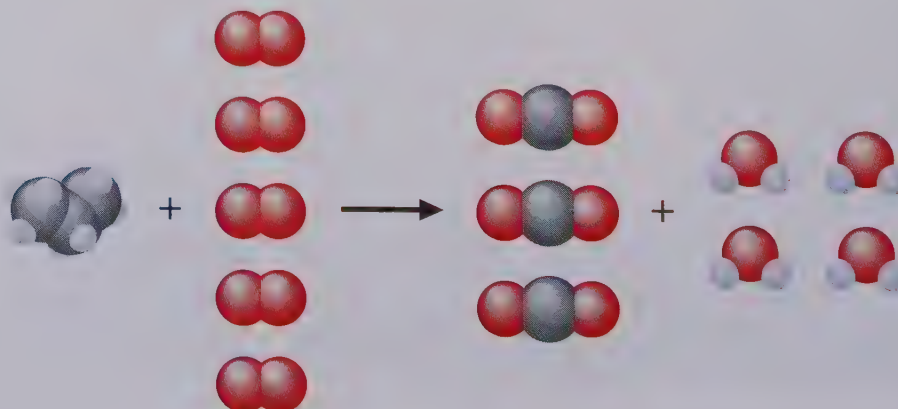
3.8 Stoichiometric Calculations: Amounts of Reactants and Products

As we have seen in previous sections of this chapter, the coefficients in chemical equations represent *numbers* of molecules, not masses of molecules. However, when a reaction is to be run in a laboratory or chemical plant, the amounts of substances needed cannot be determined by counting molecules directly. Counting is always done by weighing. In this section we will see how chemical equations can be used to determine the *masses* of reacting chemicals.

To develop the principles for dealing with the stoichiometry of reactions, we will consider the reaction of propane with oxygen to produce carbon dioxide and water. We will consider the question: “What mass of oxygen will react with 96.1 grams of propane?” In doing stoichiometry, the first thing we must do is *write the balanced chemical equation* for the reaction. In this case the balanced equation is



which can be visualized as



Before doing any calculations involving a chemical reaction, be sure the equation for the reaction is balanced.

CHEMICAL IMPACT

High Mountains—Low Octane

The next time that you visit a gas station, take a moment to note the octane rating that accompanies the grade of gasoline that you are purchasing. The gasoline is priced according to its octane rating—a measure of the fuel's antiknock properties. In a conventional internal combustion engine, gasoline vapors and air are drawn into the combustion cylinder on the downward stroke of the piston. This air–fuel mixture is compressed on the upward piston stroke (compression stroke), and a spark from the sparkplug ignites the mix. The rhythmic combustion of the fuel–air mix occurring sequentially in several cylinders furnishes the power to propel the vehicle down the road. Excessive heat and pressure (or poor-quality fuel) within the cylinder may cause the premature combustion of the mixture—commonly known as engine “knock” or “ping.” Over time, this engine knock can damage the engine, resulting in inefficient performance and costly repairs.

A consumer typically is faced with three choices of gasoline, with octane ratings of 87 (regular), 89 (midgrade), and 93 (premium). But if you happen to travel or live in the

higher elevations of the Rocky Mountain states, you might be surprised to find different octane ratings at the gasoline pumps. The reason for this provides a lesson in stoichiometry. At higher elevations the air is less dense—the volume of oxygen per unit volume of air is smaller. Most engines are designed to achieve a 14:1 oxygen-to-fuel ratio in the cylinder prior to combustion. If less oxygen is available, then less fuel is required to achieve this optimal ratio. In turn, the lower volumes of oxygen and fuel result in a lower pressure in the cylinder. Because high pressure tends to promote knocking, the lower pressure within engine cylinders at higher elevations promotes a more controlled combustion of the fuel–air mixture, and therefore, octane requirements are lower. While consumers in the Rocky Mountain states can purchase three grades of gasoline, the octane ratings of these fuel blends are different from those in the rest of the United States. In Denver, Colorado, regular gasoline is 85 octane, midgrade is 87 octane, and premium is 91 octane—2 points lower than gasoline sold in most of the rest of the country.

This equation means that 1 mole of C_3H_8 reacts with 5 moles of O_2 to produce 3 moles of CO_2 and 4 moles of H_2O . To use this equation to find the masses of reactants and products, we must be able to convert between masses and moles of substances. Thus we must first ask: “How many moles of propane are present in 96.1 grams of propane?” The molar mass of propane to three significant figures is 44.1 (that is, $3 \times 12.01 + 8 \times 1.008$). The moles of propane can be calculated as follows:

$$96.1 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol C}_3\text{H}_8}{44.1 \text{ g C}_3\text{H}_8} = 2.18 \text{ mol C}_3\text{H}_8$$

Next we must take into account the fact that each mole of propane reacts with 5 moles of oxygen. The best way to do this is to use the balanced equation to construct a **mole ratio**. In this case we want to convert from moles of propane to moles of oxygen. From the balanced equation we see that 5 moles of O_2 is required for each mole of C_3H_8 , so the appropriate ratio is

$$\frac{5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_8}$$

Multiplying the number of moles of C_3H_8 by this factor gives the number of moles of O_2 required:

$$2.18 \text{ mol C}_3\text{H}_8 \times \frac{5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_8} = 10.9 \text{ mol O}_2$$

Notice that the mole ratio is set up so that the moles of C_3H_8 cancel out, and the units that result are moles of O_2 .

Since the original question asked for the mass of oxygen needed to react with 96.1 grams of propane, the 10.9 moles of O_2 must be converted to *grams*. Since the molar mass of O_2 is 32.0 g/mol,

$$10.9 \cancel{\text{mol } O_2} \times \frac{32.0 \text{ g } O_2}{1 \cancel{\text{mol } O_2}} = 349 \text{ g } O_2$$

Therefore, 349 grams of oxygen is required to burn 96.1 grams of propane.

This example can be extended by asking: “What mass of carbon dioxide is produced when 96.1 grams of propane is combusted with oxygen?” In this case we must convert between moles of propane and moles of carbon dioxide. This can be accomplished by looking at the balanced equation, which shows that 3 moles of CO_2 is produced for each mole of C_3H_8 reacted. The mole ratio needed to convert from moles of propane to moles of carbon dioxide is

$$\frac{3 \text{ mol } CO_2}{1 \text{ mol } C_3H_8}$$

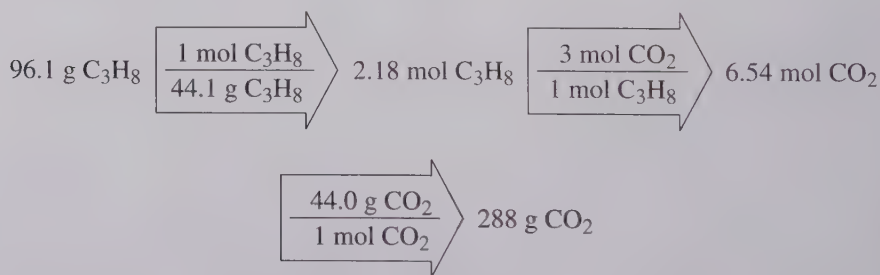
The conversion is

$$2.18 \cancel{\text{mol } C_3H_8} \times \frac{3 \text{ mol } CO_2}{1 \cancel{\text{mol } C_3H_8}} = 6.54 \text{ mol } CO_2$$

Then, using the molar mass of CO_2 (44.0 g/mol), we calculate the mass of CO_2 produced:

$$6.54 \cancel{\text{mol } CO_2} \times \frac{44.0 \text{ g } CO_2}{1 \cancel{\text{mol } CO_2}} = 288 \text{ g } CO_2$$

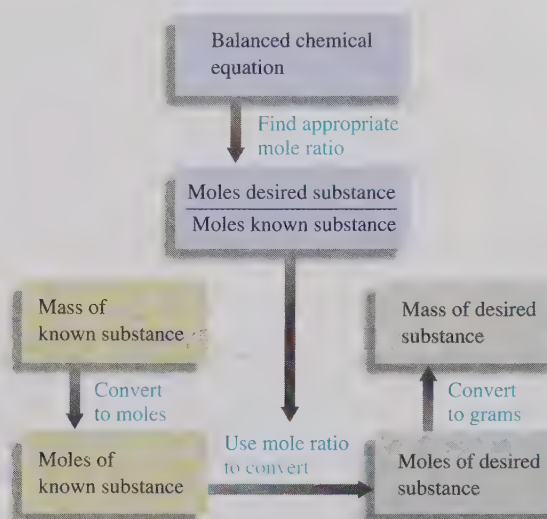
We will now summarize the sequence of steps needed to carry out stoichiometric calculations.



Calculating Masses of Reactants and Products in Chemical Reactions

- ➡ **1** Balance the equation for the reaction.
- ➡ **2** Convert the known mass of the reactant or product to moles of that substance.
- ➡ **3** Use the balanced equation to set up the appropriate mole ratios.
- ➡ **4** Use the appropriate mole ratios to calculate the number of moles of the desired reactant or product.
- ➡ **5** Convert from moles back to grams if required by the problem.

These steps are summarized by the following diagram:



SAMPLE EXERCISE 3.16



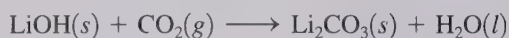
Astronaut Sidney M. Gutierrez changes the lithium hydroxide canisters on space shuttle Columbia. The lithium hydroxide is used to purge carbon dioxide from the air in the shuttle's cabin.

Chemical Stoichiometry I

Solid lithium hydroxide is used in space vehicles to remove exhaled carbon dioxide from the living environment by forming solid lithium carbonate and liquid water. What mass of gaseous carbon dioxide can be absorbed by 1.00 kg of lithium hydroxide?

SOLUTION

STEP 1 Using the description of the reaction, we can write the unbalanced equation:



The balanced equation is



STEP 2 We convert the given mass of LiOH to moles, using the molar mass of LiOH ($6.941 + 16.00 + 1.008 = 23.95 \text{ g/mol}$):

$$1.00 \text{ kg LiOH} \times \frac{1000 \text{ g LiOH}}{1 \text{ kg LiOH}} \times \frac{1 \text{ mol LiOH}}{23.95 \text{ g LiOH}} = 41.8 \text{ mol LiOH}$$

STEP 3 Since we want to determine the amount of CO_2 that reacts with the given amount of LiOH, the appropriate mole ratio is

$$\frac{1 \text{ mol CO}_2}{2 \text{ mol LiOH}}$$

STEP 4 We calculate the moles of CO_2 needed to react with the given mass of LiOH using this mole ratio:

$$41.8 \text{ mol LiOH} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol LiOH}} = 20.9 \text{ mol CO}_2$$

STEP 5 Next we calculate the mass of CO_2 , using its molar mass (44.0 g/mol):

$$20.9 \text{ mol CO}_2 \times \frac{44.0 \text{ g CO}_2}{1 \text{ mol CO}_2} = 9.20 \times 10^2 \text{ g CO}_2$$

Thus 920. g of $\text{CO}_2(\text{g})$ will be absorbed by 1.00 kg of $\text{LiOH}(\text{s})$.

See Exercises 3.85 and 3.86.

SAMPLE EXERCISE 3.17

Chemical Stoichiometry II

Baking soda (NaHCO_3) is often used as an antacid. It neutralizes excess hydrochloric acid secreted by the stomach:



Milk of magnesia, which is an aqueous suspension of magnesium hydroxide, is also used as an antacid:



Which is the more effective antacid per gram, NaHCO_3 or $\text{Mg}(\text{OH})_2$?

SOLUTION

To answer the question, we must determine the amount of HCl neutralized per gram of NaHCO_3 and per gram of $\text{Mg}(\text{OH})_2$. Using the molar mass of NaHCO_3 (84.01 g/mol), we can determine the moles of NaHCO_3 in 1.00 g of NaHCO_3 :

$$1.00 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} = 1.19 \times 10^{-2} \text{ mol NaHCO}_3$$

Next we determine the moles of HCl using the mole ratio 1 mol HCl /1 mol NaHCO_3 :

$$1.19 \times 10^{-2} \text{ mol NaHCO}_3 \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaHCO}_3} = 1.19 \times 10^{-2} \text{ mol HCl}$$

Thus 1.00 g of NaHCO_3 will neutralize 1.19×10^{-2} mol HCl .

Using the molar mass of $\text{Mg}(\text{OH})_2$ (58.32 g/mol), we determine the moles of $\text{Mg}(\text{OH})_2$ in 1.00 g:

$$1.00 \text{ g Mg}(\text{OH})_2 \times \frac{1 \text{ mol Mg}(\text{OH})_2}{58.32 \text{ g Mg}(\text{OH})_2} = 1.71 \times 10^{-2} \text{ mol Mg}(\text{OH})_2$$

To determine the moles of HCl that will react with this amount of $\text{Mg}(\text{OH})_2$, we use the mole ratio 2 mol HCl /1 mol $\text{Mg}(\text{OH})_2$:

$$1.71 \times 10^{-2} \text{ mol Mg}(\text{OH})_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Mg}(\text{OH})_2} = 3.42 \times 10^{-2} \text{ mol HCl}$$

Thus 1.00 g of $\text{Mg}(\text{OH})_2$ will neutralize 3.42×10^{-2} mol HCl . It is a better antacid per gram than NaHCO_3 .

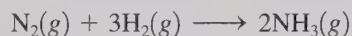
See Exercises 3.87 and 3.88.



Milk of magnesia contains a suspension of $\text{Mg}(\text{OH})_2(\text{s})$.

3.9 Calculations Involving a Limiting Reactant

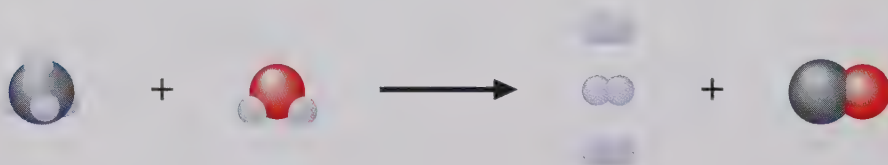
When chemicals are mixed together to undergo a reaction, they are often mixed in **stoichiometric quantities**, that is, in exactly the correct amounts so that all reactants “run out” (are used up) at the same time. To clarify this concept, let’s consider the production of hydrogen for use in the manufacture of ammonia by the **Haber process**. Ammonia, a very important fertilizer itself and a starting material for other fertilizers, is made by combining nitrogen (from the air) with hydrogen according to the equation



Hydrogen can be obtained from the reaction of methane with water vapor:



We can illustrate what we mean by stoichiometric quantities by first visualizing the balanced equation as follows:



Since this reaction involves one molecule of methane reacting with one molecule of water, to have stoichiometric amounts of methane and water we must have equal numbers of them, as shown in Fig. 3.9, where several stoichiometric mixtures are shown.

Suppose we want to calculate the mass of water required to react *exactly* with 2.50×10^3 kilograms of methane? That is, how much water will just consume all the 2.50×10^3 kilograms of methane, leaving no methane or water remaining?

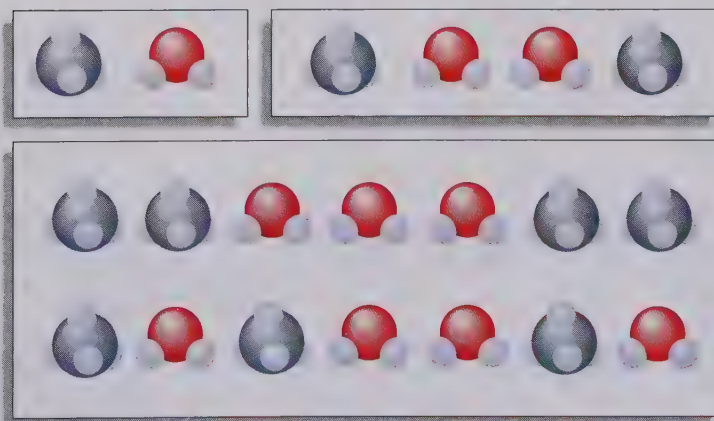


FIGURE 3.9

Three different stoichiometric mixtures of methane and water, which react one-to-one.

The details of the Haber process are discussed in Section 19.2.



Understanding Concepts: Limiting Reactants

To do this calculation, we need to recognize that we need equal numbers of methane and water molecules. Therefore, we first need to find the number of moles of methane molecules in 2.50×10^3 kg (2.50×10^6 g) of methane:

$$2.50 \times 10^6 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} = 1.56 \times 10^5 \text{ mol CH}_4 \text{ molecules}$$

↑
molar mass of CH₄

This same number of water molecules has a mass determined as follows:

$$1.56 \times 10^5 \text{ mol H}_2\text{O} \times \frac{18.02 \text{ g}}{\text{mol H}_2\text{O}} = 2.81 \times 10^6 \text{ g H}_2\text{O} = 2.81 \times 10^3 \text{ kg H}_2\text{O}$$

Thus, if 2.50×10^3 kilograms of methane is mixed with 2.81×10^3 kilograms of water, both reactants will “run out” at the same time. The reactants have been mixed in stoichiometric quantities.

If, on the other hand, 2.50×10^3 kilograms of methane is mixed with 3.00×10^3 kilograms of water, the methane will be consumed before the water runs out. The water will be in *excess*; that is, there will be more water molecules than methane molecules in the reaction mixture. What is the implication of this with respect to the number of product molecules that can form?

To answer this question, consider the situation on a smaller scale. Assume we mix 10 CH₄ molecules and 17 H₂O molecules and let them react. How many H₂ and CO molecules can form?

First picture the mixture of CH₄ and H₂O molecules as shown in Fig. 3.10.

Then imagine that groups consisting of one CH₄ molecule and one H₂O molecule (Fig. 3.10) will react to form 3 H₂ and one CO molecules (Fig. 3.11).

Notice that products can form only when both CH₄ and H₂O are available to react. Once the 10 CH₄ molecules are used up by reacting with 10 H₂O molecules, the remaining water molecules cannot react. They are in excess. Thus the number of products that can form is *limited* by the methane. Once the methane is consumed,

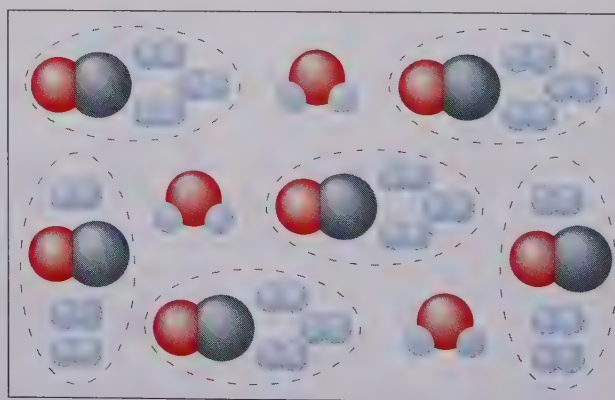
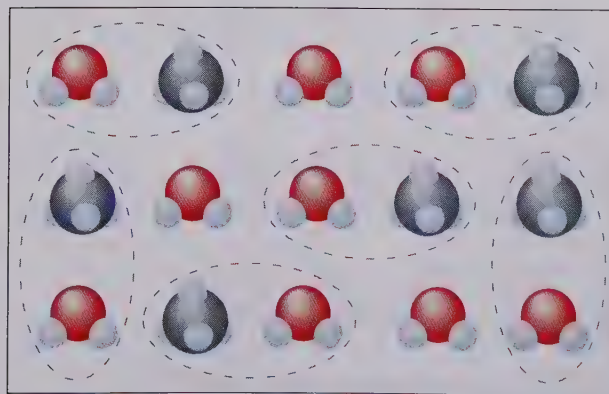
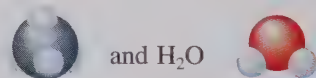
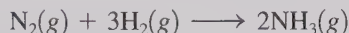


FIGURE 3.10
A mixture of CH₄ and H₂O molecules.

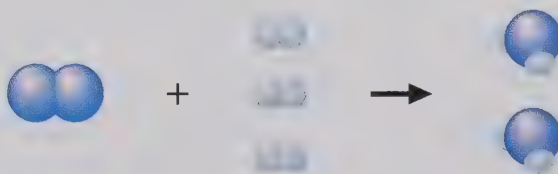
FIGURE 3.11
Methane and water have reacted to form products according to the equation $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow 3\text{H}_2 + \text{CO}$.

no more products can be formed, even though some water still remains. In this situation the amount of methane *limits* the amount of products that can be formed. This brings us to the concept of the **limiting reactant** (or **limiting reagent**), which is the reactant that is consumed first and that therefore limits the amounts of products that can be formed. In any stoichiometry calculation involving a chemical reaction, it is essential to determine which reactant is limiting so as to calculate correctly the amounts of products that will be formed.

To further explore the idea of a limiting reactant, consider the ammonia synthesis reaction:



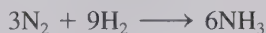
Assume that 5 N_2 molecules and 9 H_2 molecules are placed in a flask. Is this a stoichiometric mixture of reactants, or will one of them be consumed before the other runs out? From the balanced equation we know that each N_2 molecule requires 3 H_2 molecules for the reaction to occur:



Thus the required H_2/N_2 ratio is $3\text{H}_2/1\text{N}_2$. In our experiment we have 9 H_2 and 5 N_2 , or a ratio of $9\text{H}_2/5\text{N}_2 = 1.8\text{H}_2/1\text{N}_2$.

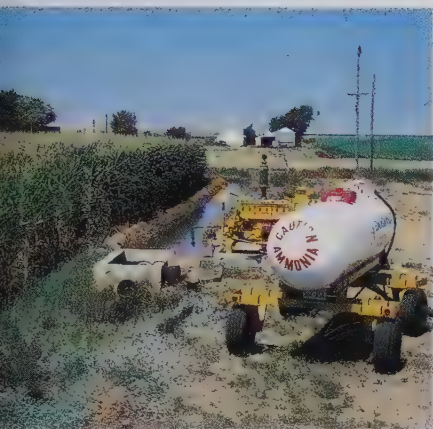
Since the actual ratio (1.8:1) of H_2/N_2 is less than the ratio required by the balanced equation (3:1), there is not enough hydrogen to react with all the nitrogen. That is, the hydrogen will run out first, leaving some unreacted N_2 molecules. We can visualize this as shown in Fig. 3.12.

Figure 3.12 shows that 3 of the N_2 molecules react with the 9 H_2 molecules to produce 6 NH_3 molecules:



This leaves 2 N_2 molecules unreacted—the nitrogen is in excess.

What we have shown here is that in this experiment the hydrogen is the limiting reactant. The amount of H_2 initially present determines the amount of NH_3 that



Ammonia is dissolved in irrigation water to provide fertilizer for a field of corn.

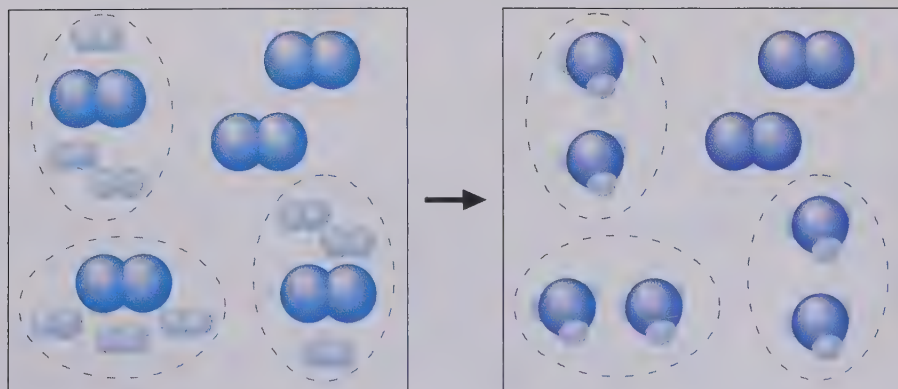
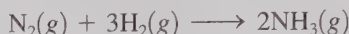


FIGURE 3.12
Hydrogen and nitrogen react to form ammonia according to the equation $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$.

can form. The reaction was not able to use up all the N_2 molecules because the H_2 molecules were all consumed by the first 3 N_2 molecules to react.

Another way to look at this is to determine how much H_2 would be required by 5 N_2 molecules. Multiplying the balanced equation



by 5 gives

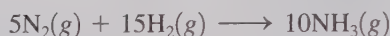


Thus 5 N_2 molecules would require 15 H_2 molecules and we have only 9. This tells us the same thing we learned earlier—the hydrogen is limiting.

The most important point here is this: *The limiting reactant limits the amount of product that can form.* The reaction that actually occurred was



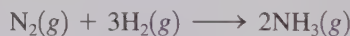
not



Thus 6 NH_3 were formed, not 10 NH_3 , because the H_2 , not the N_2 , was limiting.

In the laboratory or chemical plant we work with much larger quantities than the few molecules of the preceding example. Therefore, we must learn to deal with limiting reactants using moles. The ideas are exactly the same, except that we are using moles of molecules instead of individual molecules. For example, suppose 25.0 kilograms of nitrogen and 5.00 kilograms of hydrogen are mixed and reacted to form ammonia. How do we calculate the mass of ammonia produced when this reaction is run to completion (until one of the reactants is completely consumed)?

As in the preceding example, we must use the balanced equation



to determine whether nitrogen or hydrogen is the limiting reactant and then to determine the amount of ammonia that is formed. We first calculate the moles of reactants present:

$$25.0 \text{ kg } \text{N}_2 \times \frac{1000 \text{ g } \text{N}_2}{1 \text{ kg } \text{N}_2} \times \frac{1 \text{ mol } \text{N}_2}{28.0 \text{ g } \text{N}_2} = 8.93 \times 10^2 \text{ mol } \text{N}_2$$

$$5.00 \text{ kg } \text{H}_2 \times \frac{1000 \text{ g } \text{H}_2}{1 \text{ kg } \text{H}_2} \times \frac{1 \text{ mol } \text{H}_2}{2.016 \text{ g } \text{H}_2} = 2.48 \times 10^3 \text{ mol } \text{H}_2$$

Since 1 mol N_2 reacts with 3 mol H_2 , the number of moles of H_2 that will react exactly with 8.93×10^2 mol N_2 is

$$8.93 \times 10^2 \text{ mol } \text{N}_2 \times \frac{3 \text{ mol } \text{H}_2}{1 \text{ mol } \text{N}_2} = 2.68 \times 10^3 \text{ mol } \text{H}_2$$

Thus 8.93×10^2 mol N_2 requires 2.68×10^3 mol H_2 to react completely. However, in this case, only 2.48×10^3 mol H_2 is present. This means that the hydrogen will be consumed before the nitrogen. Thus hydrogen is the *limiting reactant* in this particular situation, and we must use the amount of hydrogen to compute the quantity of ammonia formed:

$$2.48 \times 10^3 \text{ mol } \text{H}_2 \times \frac{2 \text{ mol } \text{NH}_3}{3 \text{ mol } \text{H}_2} = 1.65 \times 10^3 \text{ mol } \text{NH}_3$$

Always determine which reactant is limiting.

Converting moles to kilograms gives

$$1.65 \times 10^3 \text{ mol } \cancel{\text{NH}_3} \times \frac{17.0 \text{ g } \text{NH}_3}{1 \text{ mol } \cancel{\text{NH}_3}} = 2.80 \times 10^4 \text{ g } \text{NH}_3 = 28.0 \text{ kg } \text{NH}_3$$

Note that to determine the limiting reactant, we could have started instead with the given amount of hydrogen and calculated the moles of nitrogen required:

$$2.48 \times 10^3 \text{ mol } \cancel{\text{H}_2} \times \frac{1 \text{ mol } \text{N}_2}{3 \text{ mol } \cancel{\text{H}_2}} = 8.27 \times 10^2 \text{ mol } \text{N}_2$$

Thus $2.48 \times 10^3 \text{ mol } \text{H}_2$ requires $8.27 \times 10^2 \text{ mol } \text{N}_2$. Since $8.93 \times 10^2 \text{ mol } \text{N}_2$ is actually present, the nitrogen is in excess. The hydrogen will run out first, and thus again we find that hydrogen limits the amount of ammonia formed.

A related but simpler way to determine which reactant is limiting is to compare the mole ratio of the substances required by the balanced equation with the mole ratio of reactants actually present. For example, in this case the mole ratio of H_2 to N_2 required by the balanced equation is

$$\frac{3 \text{ mol } \text{H}_2}{1 \text{ mol } \text{N}_2}$$

That is,

$$\frac{\text{mol } \text{H}_2}{\text{mol } \text{N}_2} (\text{required}) = \frac{3}{1} = 3$$

In this experiment we have $2.48 \times 10^3 \text{ mol } \text{H}_2$ and $8.93 \times 10^2 \text{ mol } \text{N}_2$. Thus the ratio

$$\frac{\text{mol } \text{H}_2}{\text{mol } \text{N}_2} (\text{actual}) = \frac{2.48 \times 10^3}{8.93 \times 10^2} = 2.78$$

Since 2.78 is less than 3, the actual mole ratio of H_2 to N_2 is too small, and H_2 must be limiting. If the actual H_2 to N_2 mole ratio had been greater than 3, then the H_2 would have been in excess and the N_2 would be limiting.

SAMPLE EXERCISE 3.18

Stoichiometry: Limiting Reactant

Nitrogen gas can be prepared by passing gaseous ammonia over solid copper(II) oxide at high temperatures. The other products of the reaction are solid copper and water vapor. If a sample containing 18.1 g of NH_3 is reacted with 90.4 g of CuO , which is the limiting reactant? How many grams of N_2 will be formed?

SOLUTION

From the description of the problem, we can obtain the following balanced equation:



Next we must compute the moles of NH_3 (molar mass = 17.03 g/mol) and of CuO (molar mass = 79.55 g/mol):

$$18.1 \text{ g } \cancel{\text{NH}_3} \times \frac{1 \text{ mol } \text{NH}_3}{17.03 \text{ g } \cancel{\text{NH}_3}} = 1.06 \text{ mol } \text{NH}_3$$

$$90.4 \text{ g } \cancel{\text{CuO}} \times \frac{1 \text{ mol } \text{CuO}}{79.55 \text{ g } \cancel{\text{CuO}}} = 1.14 \text{ mol } \text{CuO}$$

To determine the limiting reactant, we use the mole ratio for CuO and NH₃:

$$1.06 \text{ mol NH}_3 \times \frac{3 \text{ mol CuO}}{2 \text{ mol NH}_3} = 1.59 \text{ mol CuO}$$

Thus 1.59 mol CuO is required to react with 1.06 mol NH₃. Since only 1.14 mol CuO is actually present, the amount of CuO is limiting; CuO will run out before NH₃ does. We can verify this conclusion by comparing the mole ratio of CuO and NH₃ required by the balanced equation

$$\frac{\text{mol CuO}}{\text{mol NH}_3} (\text{required}) = \frac{3}{2} = 1.5$$

with the mole ratio actually present

$$\frac{\text{mol CuO}}{\text{mol NH}_3} (\text{actual}) = \frac{1.14}{1.06} = 1.08$$

Since the actual ratio is too small (smaller than 1.5), CuO is the limiting reactant.

Because CuO is the limiting reactant, we must use the amount of CuO to calculate the amount of N₂ formed. From the balanced equation, the mole ratio between CuO and N₂ is

$$1.14 \text{ mol CuO} \times \frac{1 \text{ mol N}_2}{3 \text{ mol CuO}} = 0.380 \text{ mol N}_2$$

Using the molar mass of N₂ (28.0 g/mol), we can calculate the mass of N₂ produced:

$$0.380 \text{ mol N}_2 \times \frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} = 10.6 \text{ g N}_2$$

See Exercises 3.95 through 3.98.

The amount of a product formed when the limiting reactant is completely consumed is called the **theoretical yield** of that product. In Sample Exercise 3.18, 10.6 grams of nitrogen represents the theoretical yield. This is the *maximum amount* of nitrogen that can be produced from the quantities of reactants used. Actually, the amount of product predicted by the theoretical yield is seldom obtained because of side reactions (other reactions that involve one or more of the reactants or products) and other complications. The *actual yield* of product is often given as a percentage of the theoretical yield. This is called the **percent yield**:

$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% = \text{percent yield}$$

For example, if the reaction considered in Sample Exercise 3.18 actually gave 6.63 grams of nitrogen instead of the predicted 10.6 grams, the percent yield of nitrogen would be

$$\frac{6.63 \text{ g N}_2}{10.6 \text{ g N}_2} \times 100\% = 62.5\%$$

Percent yield is important as an indicator of the efficiency of a particular laboratory or industrial reaction.

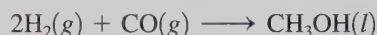
SAMPLE EXERCISE 3.19

Calculating Percent Yield

Methanol (CH_3OH), also called *methyl alcohol*, is the simplest alcohol. It is used as a fuel in race cars and is a potential replacement for gasoline. Methanol can be manufactured by combination of gaseous carbon monoxide and hydrogen. Suppose 68.5 kg CO(g) is reacted with 8.60 kg $\text{H}_2(\text{g})$. Calculate the theoretical yield of methanol. If 3.57×10^4 g CH_3OH is actually produced, what is the percent yield of methanol?

SOLUTION

First, we must find out which reactant is limiting. The balanced equation is



Next we must calculate the moles of reactants:

$$68.5 \text{ kg CO} \times \frac{1000 \text{ g CO}}{1 \text{ kg CO}} \times \frac{1 \text{ mol CO}}{28.02 \text{ g CO}} = 2.44 \times 10^3 \text{ mol CO}$$

$$8.60 \text{ kg H}_2 \times \frac{1000 \text{ g H}_2}{1 \text{ kg H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 4.27 \times 10^3 \text{ mol H}_2$$

To determine which reactant is limiting, we compare the mole ratio of H_2 and CO required by the balanced equation

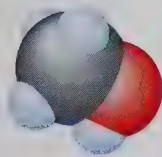
$$\frac{\text{mol H}_2}{\text{mol CO}} (\text{required}) = \frac{2}{1} = 2$$

with the actual mole ratio

$$\frac{\text{mol H}_2}{\text{mol CO}} (\text{actual}) = \frac{4.27 \times 10^3}{2.44 \times 10^3} = 1.75$$

Since the actual mole ratio of H_2 to CO is smaller than the required ratio, H_2 is *limiting*. We therefore must use the amount of H_2 and the mole ratio between H_2 and CH_3OH to determine the maximum amount of methanol that can be produced:

$$4.27 \times 10^3 \text{ mol H}_2 \times \frac{1 \text{ mol CH}_3\text{OH}}{2 \text{ mol H}_2} = 2.14 \times 10^3 \text{ mol CH}_3\text{OH}$$



Methanol.

Methanol is used as a fuel in Indianapolis-type racing cars.

Using the molar mass of CH_3OH (32.04 g/mol), we can calculate the theoretical yield in grams:

$$2.14 \times 10^3 \text{ mol } \text{CH}_3\text{OH} \times \frac{32.04 \text{ g } \text{CH}_3\text{OH}}{1 \text{ mol } \text{CH}_3\text{OH}} = 6.86 \times 10^4 \text{ g } \text{CH}_3\text{OH}$$

Thus, from the amount of reactants given, the maximum amount of CH_3OH that can be formed is $6.86 \times 10^4 \text{ g}$. This is the *theoretical yield*.

The percent yield is

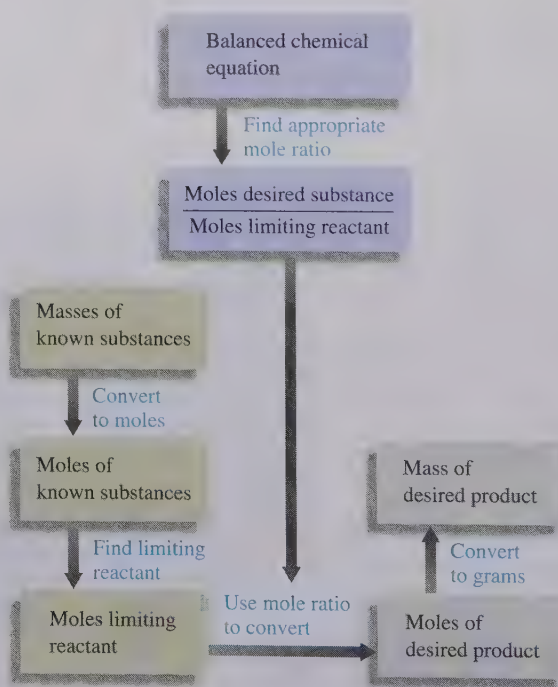
$$\frac{\text{Actual yield (grams)}}{\text{Theoretical yield (grams)}} \times 100 = \frac{3.57 \times 10^4 \text{ g } \text{CH}_3\text{OH}}{6.86 \times 10^4 \text{ g } \text{CH}_3\text{OH}} \times 100\% = 52.0\%$$

See Exercises 3.99 and 3.100.

Solving a Stoichiometry Problem Involving Masses of Reactants and Products

- ➡ **1** Write and balance the equation for the reaction.
- ➡ **2** Convert the known masses of substances to moles.
- ➡ **3** Determine which reactant is limiting.
- ➡ **4** Using the amount of the limiting reactant and the appropriate mole ratios, compute the number of moles of the desired product.
- ➡ **5** Convert from moles to grams, using the molar mass.

This process is summarized in the diagram below:



For Review

Summary

Stoichiometry deals with the quantities of materials consumed and produced in chemical reactions. It is, in effect, chemical arithmetic. The average atomic mass for each element is obtained by computing the average of the masses of the naturally occurring isotopes. All atomic masses are based on a mass scale that assigns exactly 12 atomic mass units to a ^{12}C atom.

A mole is a unit of measure equal to the number of carbon atoms in exactly 12 grams of pure ^{12}C . This number has been determined experimentally to be 6.02214×10^{23} , which is called Avogadro's number. One mole of any substance contains Avogadro's number of units. One mole of an element has a mass equal to the element's atomic mass in grams.

The molar mass (molecular weight) of a compound is the mass in grams of one mole of the compound and is computed by summing the average masses of its constituent atoms.

Percent composition represents the mass percent of each element in a compound:

$$\text{Mass percent} = \frac{\text{mass of element in 1 mole of substance}}{\text{mass of 1 mole of substance}} \times 100\%$$

The empirical formula is the simplest whole-number ratio of the various types of atoms in a compound and can be derived from the percent composition of the compound. The molecular formula is the exact formula of a molecule of a substance and is always an integer multiple of the empirical formula.

In a chemical reaction, atoms are neither created nor destroyed; they are merely reorganized. All atoms present in the reactants must be accounted for among the products. A chemical equation represents the chemical reaction showing reactants on the left side of an arrow and products on the right. A balanced equation gives the relative numbers of reactant and product molecules.

Amounts of reactants consumed and products formed can be calculated from the balanced equation for a reaction by using the mole ratios relating the reactants and products. The limiting reactant (reagent) is the one that is consumed first and thus determines how much product can be formed.

The theoretical yield of a product is the maximum amount that can be produced from a given amount of the limiting reactant. The actual yield, the amount of product actually obtained in a given experiment, is always less than the theoretical yield. The actual yield is usually represented as a percent yield: the percentage of the theoretical yield actually obtained.

Key Terms

chemical stoichiometry

Section 3.1

mass spectrometer

average atomic mass

Section 3.2

mole

Avogadro's number

Section 3.3

molar mass

Section 3.4

mass percent

Section 3.5

empirical formula

molecular formula

Section 3.6

chemical equation

reactants

products

balancing a chemical equation

Section 3.8

mole ratio

Section 3.9

stoichiometric quantities

Haber process

limiting reactant (reagent)

theoretical yield

percent yield

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. The following are actual student responses to the question: Why is it necessary to balance chemical equations?

- a. The chemicals will not react until you have added the correct mole ratios.
- b. The correct products will not be formed unless the right amount of reactants have been added.
- c. A certain number of products cannot be formed without a certain number of reactants.
- d. The balanced equation tells you how much reactant you need and allows you to predict how much product you'll make.

e. A mole-to-mole ratio must be established for the reaction to occur as written.

Justify the best choice, and for choices you did not pick, explain what is wrong with them.

2. What information do we get from a formula? From an equation?

3. You are making cookies and are missing a key ingredient—eggs. You have most of the other ingredients needed to make the cookies, except you have only 1.33 cups of butter and no eggs. You note that the recipe calls for 2 cups of butter and 3 eggs (plus the other ingredients) to make 6 dozen cookies. You call a friend and have him bring you some eggs.

a. How many eggs do you need?

b. If you use all the butter (and get enough eggs), how many cookies will you make?

Unfortunately, your friend hangs up before you tell him how many eggs you need. When he arrives, he has a surprise for you—to save time, he has broken them all in a bowl for you. You ask him how many he brought, and he replies, “I can’t remember.” You weigh the eggs and find that they weigh 62.1 g. Assuming that an average egg weighs 34.21 g,

a. How much butter is needed to react with all the eggs?

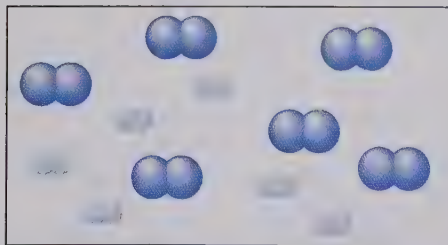
b. How many cookies can you make?

c. Which will you have left over, eggs or butter?

d. How much is left over?

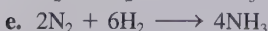
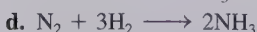
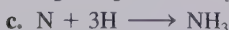
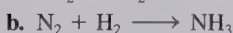
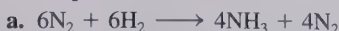
4. Nitrogen (N_2) and hydrogen (H_2) react to form ammonia (NH_3).

Consider the mixture of N_2 () and H_2 () in a closed container as illustrated below:



Assuming the reaction goes to completion, draw a representation of the product mixture. Explain how you arrived at this representation.

5. For the preceding question, which of the following equations best represents the reaction?

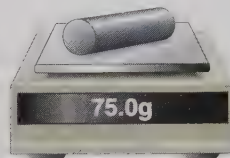


Justify your choice, and for choices you did not pick, explain what is wrong with them.

6. You know that chemical A reacts with chemical B. You react 10.0 g A with 10.0 g B. What information do you need to determine the amount of product that will be produced? Explain.

7. A new grill has a mass of 30.0 kg. You put 3.0 kg of charcoal in the grill. You burn all the charcoal and the grill has a mass of 30.0 kg. What is the mass of the gases given off? Explain.

8. Consider an iron bar on a balance as shown.



As the iron bar rusts, which of the following is true? Explain your answer.

a. The balance will read less than 75.0 g.

b. The balance will read 75.0 g.

c. The balance will read greater than 75.0 g.

d. The balance will read greater than 75.0 g, but if the bar is removed, the rust is scraped off, and the bar replaced, the balance will read 75.0 g.

9. You may have noticed that water sometimes drips from the exhaust of a car as it is running. Is this evidence that there is at least a small amount of water originally present in the gasoline? Explain.

Questions 10 and 11 deal with the following situation: You react chemical A with chemical B to make one product. It takes 100 g of A to react completely with 20 g B.

10. What is the mass of the product?

a. Less than 10 g

b. Between 20 and 100 g

c. Between 100 and 120 g

d. Exactly 120 g

e. More than 120 g

11. What is true about the chemical properties of the product?

a. The properties are more like chemical A.

b. The properties are more like chemical B.

c. The properties are an average of those of chemical A and chemical B.

d. The properties are not necessarily like either chemical A or chemical B.

e. The properties are more like chemical A or more like chemical B, but more information is needed.

Justify your choice, and for choices you did not pick, explain what is wrong with them.

12. Is there a difference between a homogeneous mixture of hydrogen and oxygen in a 2:1 mole ratio and a sample of water vapor? Explain.

13. Chlorine exists mainly as two isotopes, ^{37}Cl and ^{35}Cl . Which is more abundant? How do you know?

14. The average mass of a carbon atom is 12.011. Assuming you could pick up one carbon atom, estimate the chance that you would randomly get one with a mass of 12.011. Support your answer.

15. Can the subscripts in a chemical formula be fractions? Explain. Can the coefficients in a balanced chemical equation be fractions? Explain. Changing the subscripts of chemicals can balance the equations mathematically. Why is this unacceptable?
16. Consider the equation $2A + B \longrightarrow A_2B$. If you mix 1.0 mol of A with 1.0 mol of B , how many moles of A_2B can be produced?
17. According to the law of conservation of mass, mass cannot be gained or destroyed in a chemical reaction. Why can't you simply add the masses of two reactants to determine the total mass of product?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

Questions

18. The atomic mass of boron (B) is given in the periodic table as 10.81, yet no single atom of boron has a mass of 10.81 amu. Explain.
19. What is the difference between the empirical and molecular formulas of a compound? Can they ever be the same? Explain.
20. Why is the actual yield of a reaction often less than the theoretical yield?

Exercises

In this section similar exercises are paired.

Atomic Masses and the Mass Spectrometer

21. The element magnesium (Mg) has three stable isotopes with the following masses and abundances:

Isotope	Mass (amu)	Abundance
^{24}Mg	23.9850	78.99%
^{25}Mg	24.9858	10.00%
^{26}Mg	25.9826	11.01%

Calculate the average atomic mass (the atomic weight) of magnesium from these data.

22. An element consists of 1.40% of an isotope with mass 203.973 amu, 24.10% of an isotope with mass 205.9745 amu, 22.10% of an isotope with mass 206.9759 amu, and 52.40% of an isotope with mass 207.9766 amu. Calculate the average atomic mass and identify the element.
23. The element europium exists in nature as two isotopes: ^{151}Eu has a mass of 150.9196 amu, and ^{153}Eu has a mass of 152.9209 amu. The average atomic mass of europium is 151.96 amu. Calculate the relative abundance of the two europium isotopes.

24. The element rhenium (Re) has two naturally occurring isotopes, ^{185}Re and ^{187}Re , with an average atomic mass of 186.207 amu. Rhenium is 62.60% ^{187}Re , and the atomic mass of ^{187}Re is 186.956 amu. Calculate the mass of ^{185}Re .
25. The mass spectrum of bromine (Br_2) consists of three peaks with the following characteristics:

Mass (amu)	Relative Size
157.84	0.2534
159.84	0.5000
161.84	0.2466

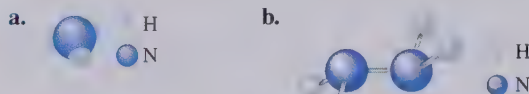
How do you interpret these data?

26. Gallium arsenide, GaAs, has gained widespread use in semiconductor devices that convert light and electrical signals in fiber-optic communications systems. Gallium consists of 60.4% ^{69}Ga and 39.6% ^{71}Ga . Arsenic has only one naturally occurring isotope, ^{75}As . Gallium arsenide is a polymeric material, but its mass spectrum shows fragments with the formulas GaAs and Ga_2As_2 . What would the distribution of peaks look like for these two fragments?

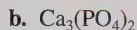
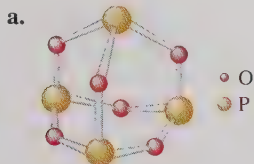
Moles and Molar Masses

27. Calculate the mass of 500. atoms of iron (Fe).
28. How many Fe atoms and how many moles of Fe atoms are in 500.0 g of iron?
29. Diamond is a natural form of pure carbon. How many atoms of carbon are in a 1.00-carat diamond (1.00 carat = 0.200 g)?
30. A diamond contains 5.0×10^{21} atoms of carbon. How many moles of carbon and how many grams of carbon are in this diamond?
31. Aluminum metal is produced by passing an electric current through a solution of aluminum oxide (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). Calculate the molar masses of Al_2O_3 and Na_3AlF_6 .
32. The Freons are a class of compounds containing carbon, chlorine, and fluorine. While they have many valuable uses, they have been shown to be responsible for depletion of the ozone in the upper atmosphere. In 1991, two replacement compounds for Freons went into production: HFC-134a (CH_2FCF_3) and HCFC-124 (CHClFCF_3). Calculate the molar masses of these two compounds.

33. Calculate the molar mass of the following substances.



34. Calculate the molar mass of the following substances.



35. How many moles of compound are present in 1.00 g of each of the compounds in Exercise 33?

36. How many moles of compound are present in 1.00 g of each of the compounds in Exercise 34?

37. How many grams of compound are present in 5.00 mol of each of the compounds in Exercise 33?

38. How many grams of compound are present in 5.00 mol of each of the compounds in Exercise 34?

39. How many grams of nitrogen are present in 5.00 mol of each of the compounds in Exercise 33?

40. How many grams of phosphorus are present in 5.00 mol of each of the compounds in Exercise 34?

41. How many molecules (or formula units) are present in 1.00 g of each of the compounds in Exercise 33?

42. How many molecules (or formula units) are present in 1.00 g of each of the compounds in Exercise 34?

43. How many atoms of nitrogen are present in 1.00 g of each of the compounds in Exercise 33?

44. How many atoms of phosphorus are present in 1.00 g of each of the compounds in Exercise 34?

45. Ascorbic acid, or vitamin C ($\text{C}_6\text{H}_8\text{O}_6$), is an essential vitamin. It cannot be stored by the body and must be present in the diet. What is the molar mass of ascorbic acid? Vitamin C tablets are taken as a dietary supplement. If a typical tablet contains 500.0 mg of vitamin C, how many moles and how many molecules of vitamin C does it contain?

46. The molecular formula of acetylsalicylic acid (aspirin), one of the most commonly used pain relievers, is $\text{C}_9\text{H}_8\text{O}_4$.

a. Calculate the molar mass of aspirin.

b. A typical aspirin tablet contains 500. mg of $\text{C}_9\text{H}_8\text{O}_4$. How many moles of $\text{C}_9\text{H}_8\text{O}_4$ molecules and how many molecules of acetylsalicylic acid are in a 500.-mg tablet?

47. How many moles are represented by each of these samples?

a. 2.49×10^{20} molecules of carbon monoxide

b. 15.0 g of copper(II) sulfate

c. 100 molecules (exactly) of sulfuric acid

d. 6.210 mg of potassium oxide

48. How many moles are represented by each of these samples?

a. 150.0 g Fe_2O_3 c. 1.5×10^{16} molecules of BF_3

b. 10.0 mg NO_2

49. Calculate the mass in grams of the following:

a. 1.27 mmol of carbon dioxide

b. 2.00×10^{22} molecules of nitrogen trichloride

c. 0.00451 mol of ammonium carbonate

d. a single nitrogen (N_2) molecule

e. 62.7 mol of copper(II) sulfate

50. How many atoms of nitrogen are present in 5.00 g of each of the following?

a. glycine, $\text{C}_2\text{H}_5\text{O}_2\text{N}$

c. calcium nitrate

b. magnesium nitride

d. dinitrogen tetroxide

51. Aspartame is an artificial sweetener that is 160 times sweeter than sucrose (table sugar) when dissolved in water. It is marketed as Nutra-Sweet. The molecular formula of aspartame is $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$.

a. Calculate the molar mass of aspartame.

b. How many moles of molecules are present in 10.0 g aspartame?

c. Calculate the mass in grams of 1.56 mol aspartame.

d. How many molecules are in 5.0 mg aspartame?

e. How many atoms of nitrogen are in 1.2 g aspartame?

f. What is the mass in grams of 1.0×10^9 molecules of aspartame?

g. What is the mass in grams of one molecule of aspartame?

52. Chloral hydrate ($\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$) is a drug formerly used as a sedative and hypnotic. It is the compound used to make "Mickey Finns" in detective stories.

a. Calculate the molar mass of chloral hydrate.

b. How many moles of $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$ molecules are in 500.0 g chloral hydrate?

c. What is the mass in grams of 2.0×10^{-2} mol chloral hydrate?

d. How many chlorine atoms are in 5.0 g chloral hydrate?

e. What mass of chloral hydrate would contain 1.0 g Cl?

f. What is the mass of exactly 500 molecules of chloral hydrate?

Percent Composition

53. In 1987 the first substance to act as a superconductor at a temperature above that of liquid nitrogen (77 K) was discovered. The approximate formula of this substance is $\text{YBa}_2\text{Cu}_3\text{O}_7$. Calculate the percent composition by mass of this material.

54. Calculate the percent composition by mass of the following compounds that are important starting materials for synthetic polymers:

a. $\text{C}_3\text{H}_4\text{O}_2$ (acrylic acid, from which acrylic plastics are made)

b. $\text{C}_4\text{H}_6\text{O}_2$ (methyl acrylate, from which Plexiglas is made)

c. $\text{C}_3\text{H}_3\text{N}$ (acrylonitrile, from which Orlon is made)

55. Several important compounds contain only nitrogen and oxygen. Place the following compounds in order of increasing mass percent of nitrogen.

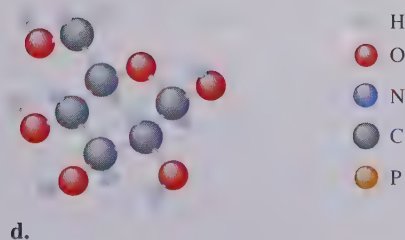
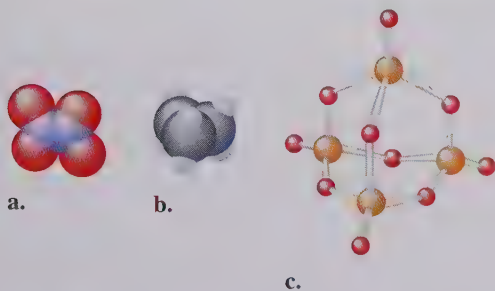
a. NO , a gas formed by the reaction of N_2 with O_2 in internal combustion engines

b. NO_2 , a brown gas mainly responsible for the brownish color of photochemical smog

- c. N_2O_4 , a colorless liquid used as fuel in space shuttles
 d. N_2O , a colorless gas sometimes used as an anesthetic by dentists (known as laughing gas)
56. Arrange the following substances in order of increasing mass percent of carbon.
 a. caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
 b. sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 c. ethanol, $\text{C}_2\text{H}_5\text{OH}$
57. Vitamin B_{12} , cyanocobalamin, is essential for human nutrition. It is concentrated in animal tissue but not in higher plants. Although nutritional requirements for the vitamin are quite low, people who abstain completely from animal products may develop a deficiency anemia. Cyanocobalamin is the form used in vitamin supplements. It contains 4.34% cobalt by mass. Calculate the molar mass of cyanocobalamin, assuming that there is one atom of cobalt in every molecule of cyanocobalamin.
58. Fungal laccase, a blue protein found in wood-rotting fungi, is 0.390% Cu by mass. If a fungal laccase molecule contains 4 copper atoms, what is the molar mass of fungal laccase?

Empirical and Molecular Formulas

59. Express the composition of each of the following compounds as the mass percents of its elements.
 a. formaldehyde, CH_2O
 b. glucose, $\text{C}_6\text{H}_{12}\text{O}_6$
 c. acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$
60. Considering your answer to Exercise 59, which type of formula, empirical or molecular, can be obtained from elemental analysis that gives percent composition?
61. Give the empirical formula for each of the compounds represented below.



62. Determine the molecular formulas to which the following empirical formulas and molar masses pertain.
 a. SNH (188.35 g/mol)
 b. NPCl_2 (347.64 g/mol)
 c. CoC_4O_4 (341.94 g/mol)
 d. SN (184.32 g/mol)
63. One of the most commonly used white pigments in paint is a compound of titanium and oxygen that contains 59.9% Ti by mass. Determine the empirical formula of this compound.
64. The compound adrenaline contains 56.79% C, 6.56% H, 28.37% O, and 8.28% N by mass. What is the empirical formula for adrenaline?
65. There are two binary compounds of mercury and oxygen. Heating either of them results in the decomposition of the compound, with oxygen gas escaping into the atmosphere while leaving a residue of pure mercury. Heating 0.6498 g of one of the compounds leaves a residue of 0.6018 g. Heating 0.4172 g of the other compound results in a mass loss of 0.016 g. Determine the empirical formula of each compound.
66. A sample of urea contains 1.121 g N, 0.161 g H, 0.480 g C, and 0.640 g O. What is the empirical formula of urea?
67. A compound that contains only nitrogen and oxygen is 30.4% N by mass; the molar mass of the compound is 92 g/mol. What is the empirical formula of the compound? What is the molecular formula of the compound?
68. A compound containing only sulfur and nitrogen is 69.6% S by mass; the molar mass is 184 g/mol. What are the empirical and molecular formulas of the compound?
69. Adipic acid is an organic compound composed of 49.31% C, 43.79% O, and the rest hydrogen. If the molar mass of adipic acid is 146.1 g/mol, what are the empirical and molecular formulas for adipic acid?
70. Maleic acid is an organic compound composed of 41.39% C, 3.47% H, and the rest oxygen. If 0.129 mol of maleic acid has a mass of 15.0 g, what are the empirical and molecular formulas of maleic acid?
71. Many homes in rural America are heated by propane gas, a compound that contains only carbon and hydrogen. Complete combustion of a sample of propane produced 2.641 g of carbon dioxide and 1.442 g of water as the only products. Find the empirical formula of propane.
72. A compound contains only C, H, and N. Combustion of 35.0 mg of the compound produces 33.5 mg CO_2 and 41.1 mg H_2O . What is the empirical formula of the compound?
73. Cumene is a compound containing only carbon and hydrogen that is used in the production of acetone and phenol in the chemical industry. Combustion of 47.6 mg cumene produces some CO_2 and 42.8 mg water. The molar mass of cumene is between 115 and 125 g/mol. Determine the empirical and molecular formulas.

74. A compound contains only carbon, hydrogen, and oxygen. Combustion of 10.68 mg of the compound yields 16.01 mg CO_2 and 4.37 mg H_2O . The molar mass of the compound is 176.1 g/mol. What are the empirical and molecular formulas of the compound?

Balancing Chemical Equations

75. Write a balanced chemical equation that describes each of the following.
- Iron metal reacts with oxygen to form rust, iron(III) oxide.
 - Calcium metal reacts with water to produce aqueous calcium hydroxide and hydrogen gas.
 - Aqueous barium hydroxide reacts with aqueous sulfuric acid to produce solid barium sulfate and water.
76. Give the balanced equation for each of the following chemical reactions:
- Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) reacts with oxygen gas to produce gaseous carbon dioxide and water vapor.
 - Solid iron(III) sulfide reacts with gaseous hydrogen chloride to form solid iron(III) chloride and hydrogen sulfide gas.
 - Carbon disulfide liquid reacts with ammonia gas to produce hydrogen sulfide gas and solid ammonium thiocyanate (NH_4SCN).

77. Balance the following equations:

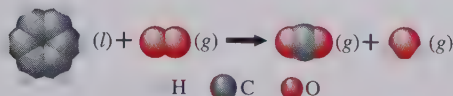
- $\text{Cu}(s) + \text{AgNO}_3(aq) \rightarrow \text{Ag}(s) + \text{Cu}(\text{NO}_3)_2(aq)$
- $\text{Zn}(s) + \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$
- $\text{Au}_2\text{S}_3(s) + \text{H}_2(g) \rightarrow \text{Au}(s) + \text{H}_2\text{S}(g)$

78. Balance the following equations:

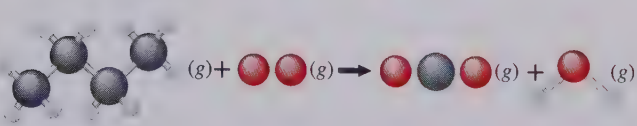
- $\text{Ca}(\text{OH})_2(aq) + \text{H}_3\text{PO}_4(aq) \rightarrow \text{H}_2\text{O}(l) + \text{Ca}_3(\text{PO}_4)_2(s)$
- $\text{Al}(\text{OH})_3(s) + \text{HCl}(aq) \rightarrow \text{AlCl}_3(aq) + \text{H}_2\text{O}(l)$
- $\text{AgNO}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Ag}_2\text{SO}_4(s) + \text{HNO}_3(aq)$

79. Balance the following equations representing combustion reactions:

a.



b.



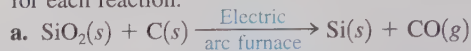
- $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g)$
- $\text{Fe}(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$
- $\text{FeO}(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$

80. Balance the following equations:

- $\text{Cr}(s) + \text{S}_8(s) \rightarrow \text{Cr}_2\text{S}_3(s)$
- $\text{NaHCO}_3(s) \xrightarrow{\text{Heat}} \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$

- $\text{KClO}_3(s) \xrightarrow{\text{Heat}} \text{KCl}(s) + \text{O}_2(g)$
- $\text{Eu}(s) + \text{HF}(g) \rightarrow \text{EuF}_3(s) + \text{H}_2(g)$

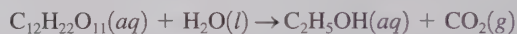
81. Silicon is produced for the chemical and electronics industries by the following reactions. Give the balanced equation for each reaction.



- Silicon tetrachloride is reacted with very pure magnesium, producing silicon and magnesium chloride.
- $\text{Na}_2\text{SiF}_6(s) + \text{Na}(s) \rightarrow \text{Si}(s) + \text{NaF}(s)$

82. Phosphorus occurs naturally in the form of fluorapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, the dot indicating 1 part CaF_2 to 3 parts $\text{Ca}_3(\text{PO}_4)_2$. This mineral is reacted with an aqueous solution of sulfuric acid in the preparation of a fertilizer. The products are phosphoric acid, hydrogen fluoride, and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Write and balance the chemical equation describing this process.

83. The sugar sucrose, which is present in many fruits and vegetables, reacts in the presence of certain yeast enzymes to produce ethyl alcohol (ethanol) and carbon dioxide gas. Balance the following equation for this reaction of sucrose.



84. Glass is a mixture of several compounds, but a major constituent of most glass is calcium silicate, CaSiO_3 . Glass can be etched by treatment with hydrofluoric acid; HF attacks the calcium silicate of the glass, producing gaseous and water-soluble products (which can be removed by washing the glass). For example, the volumetric glassware in chemistry laboratories is often graduated by using this process. Balance the following equation for the reaction of hydrofluoric acid with calcium silicate.



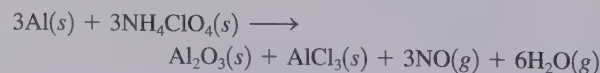
Reaction Stoichiometry

- Calculate the masses of Cr_2O_3 , N_2 , and H_2O produced from 10.8 g $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in an ammonium dichromate volcano reaction as described in Sample Exercise 3.14.
- Over the years, the thermite reaction has been used for welding railroad rails, in incendiary bombs, and to ignite solid-fuel rocket motors. The reaction is



What masses of iron(III) oxide and aluminum must be used to produce 15.0 g iron? What is the maximum mass of aluminum oxide that could be produced?

87. The reusable booster rockets of the U.S. space shuttle employ a mixture of aluminum and ammonium perchlorate for fuel. A possible equation for this reaction is



What mass of NH_4ClO_4 should be used in the fuel mixture for every kilogram of Al?

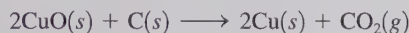
88. One of relatively few reactions that takes place directly between two solids at room temperature is



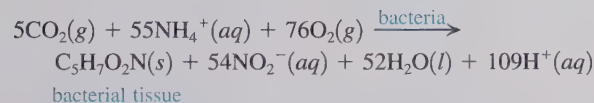
In this equation, the $\cdot 8\text{H}_2\text{O}$ in $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ indicates the presence of eight water molecules. This compound is called barium hydroxide octahydrate.

- Balance the equation.
- What mass of ammonium thiocyanate (NH_4SCN) must be used if it is to react completely with 6.5 g barium hydroxide octahydrate?

89. Coke is an impure form of carbon that is often used in the industrial production of metals from their oxides. If a sample of coke is 95% carbon by mass, determine the mass of coke needed to react completely with 1.0 ton of copper(II) oxide.



90. Bacterial digestion is an economical method of sewage treatment. The reaction



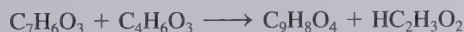
is an intermediate step in the conversion of the nitrogen in organic compounds into nitrate ions. How much bacterial tissue is produced in a treatment plant for every 1.0×10^4 kg of wastewater containing 3.0% NH_4^+ ions by mass? Assume that 95% of the ammonium ions are consumed by the bacteria.

91. The compound cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, has been studied extensively as an antitumor agent.
- Calculate the elemental percent composition by mass of cisplatin.
 - Cisplatin is synthesized as follows:



What mass of cisplatin can be made from 100. g of K_2PtCl_4 and sufficient NH_3 ? What mass of KCl is also produced?

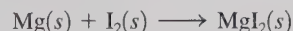
92. Aspirin ($\text{C}_9\text{H}_8\text{O}_4$) is synthesized by reacting salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) with acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$). The balanced equation is



- What mass of acetic anhydride is needed to completely consume 1.00×10^2 g salicylic acid?
- What is the maximum mass of aspirin (the theoretical yield) that could be produced in this reaction?

Limiting Reactants and Percent Yield

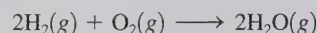
93. Consider the reaction



Identify the limiting reagent in each of the reaction mixtures below:

- 100 atoms of Mg and 100 molecules of I_2
- 150 atoms of Mg and 100 molecules of I_2
- 200 atoms of Mg and 300 molecules of I_2
- 0.16 mol Mg and 0.25 mol I_2
- 0.14 mol Mg and 0.14 mol I_2
- 0.12 mol Mg and 0.08 mol I_2
- 6.078 g Mg and 63.46 g I_2
- 1.00 g Mg and 2.00 g I_2
- 1.00 g Mg and 20.00 g I_2

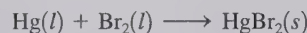
94. Consider the reaction



Identify the limiting reagent in each of the reaction mixtures given below:

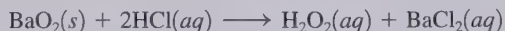
- 50 molecules of H_2 and 25 molecules of O_2
- 100 molecules of H_2 and 40 molecules of O_2
- 100 molecules of H_2 and 100 molecules of O_2
- 0.50 mol H_2 and 0.75 mol O_2
- 0.80 mol H_2 and 0.75 mol O_2
- 1.0 g H_2 and 0.25 mol O_2
- 5.00 g H_2 and 56.00 g O_2

95. Mercury and bromine will react with each other to produce mercury(II) bromide:



- What mass of HgBr_2 can be produced from the reaction of 10.0 g Hg and 9.00 g Br_2 ? What mass of which reagent is left unreacted?
- What mass of HgBr_2 can be produced from the reaction of 5.00 mL mercury (density = 13.6 g/mL) and 5.00 mL bromine (density = 3.10 g/mL)?

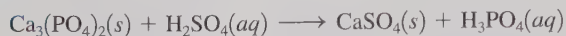
96. Hydrogen peroxide is used as a cleaning agent in the treatment of cuts and abrasions for several reasons. It is an oxidizing agent that can directly kill many microorganisms; it decomposes upon contact with blood, releasing elemental oxygen gas (which inhibits the growth of anaerobic microorganisms); and it foams upon contact with blood, which provides a cleansing action. In the laboratory, small quantities of hydrogen peroxide can be prepared by the action of an acid on an alkaline earth metal peroxide, such as barium peroxide:



What amount of hydrogen peroxide should result when 1.50 g of barium peroxide is treated with 25.0 mL of hy-

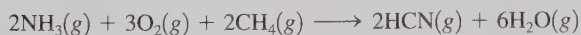
drochloric acid solution containing 0.0272 g of HCl per mL? What mass of which reagent is left unreacted?

97. Consider the following unbalanced equation:



What masses of calcium sulfate and phosphoric acid can be produced from the reaction of 1.0 kg calcium phosphate with 1.0 kg concentrated sulfuric acid (98% H_2SO_4 by mass)?

98. Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen, and methane:

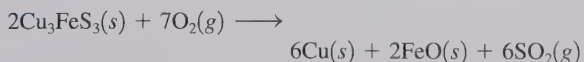


If 5.00×10^3 kg each of NH_3 , O_2 , and CH_4 are reacted, what mass of HCN and of H_2O will be produced, assuming 100% yield?

99. The reaction of ethane gas (C_2H_6) with chlorine gas produces $\text{C}_2\text{H}_5\text{Cl}$ as its main product (along with HCl). In addition, the reaction invariably produces a variety of other minor products, including $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_3\text{Cl}_3$, and others. Naturally, the production of these minor products reduces the yield of the main product. Calculate the percent yield of $\text{C}_2\text{H}_5\text{Cl}$ if the reaction of 300. g of ethane with 650. g of chlorine produced 490. g of $\text{C}_2\text{H}_5\text{Cl}$.

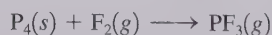
100. A student prepared aspirin in a laboratory experiment using the reaction in Exercise 92. The student reacted 1.50 g salicylic acid with 2.00 g acetic anhydride. The yield was 1.50 g aspirin. Calculate the theoretical yield and the percent yield for this experiment.

101. Bornite (Cu_3FeS_3) is a copper ore used in the production of copper. When heated, the following reaction occurs:



If 2.50 metric tons of bornite is reacted with excess O_2 and the process has an 86.3% yield of copper, how much copper is produced?

102. Consider the following unbalanced reaction:



How many grams of F_2 are needed to produce 120. g of PF_3 if the reaction has a 78.1% yield?

duced at the rate of 1000. kg/h. How much water must be evaporated per hour if the final product contains only 20.% water?

105. The empirical formula of styrene is CH ; the molar mass of styrene is 104.14 g/mol. How many H atoms are present in a 2.00-g sample of styrene?
106. Terephthalic acid is an important chemical used in the manufacture of polyesters and plasticizers. It contains only C, H, and O. Combustion of 19.81 mg terephthalic acid produces 41.98 mg CO_2 and 6.45 mg H_2O . If 0.250 mol of terephthalic acid has a mass of 41.5 g, determine the molecular formula for terephthalic acid.
107. A sample of a hydrocarbon (a compound consisting of only carbon and hydrogen) contains 2.59×10^{23} atoms of hydrogen and is 17.3% hydrogen by mass. If the molar mass of the hydrocarbon is between 55 and 65 g/mol, how many mol of compound are present, and what is the mass of the sample?
108. A binary compound between an unknown element E and hydrogen contains 91.27% E and 8.73% H by mass. If the formula of the compound is E_3H_8 , calculate the atomic mass of E.

109. A 0.755-g sample of hydrated copper(II) sulfate



was heated carefully until it had changed completely to anhydrous copper(II) sulfate (CuSO_4) with a mass of 0.483 g. Determine the value of x . (This number is called the *number of waters of hydration* of copper(II) sulfate. It specifies the number of water molecules per formula unit of CuSO_4 in the hydrated crystal.)

110. ABS plastic is a tough, hard plastic used in applications requiring shock resistance. The polymer consists of three monomer units: acrylonitrile ($\text{C}_3\text{H}_3\text{N}$), butadiene (C_4H_6), and styrene (C_8H_8).
- a. A sample of ABS plastic contains 8.80% N by mass. It took 0.605 g of Br_2 to react completely with a 1.20-g sample of ABS plastic. Bromine reacts 1:1 (by moles) with the butadiene molecules in the polymer and nothing else. What is the percent by mass of acrylonitrile and butadiene in this polymer?
- b. What are the relative numbers of each of the monomer units in this polymer?

111. A sample of LSD (D-lysergic acid diethylamide, $\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}$) is added to some table salt (sodium chloride) to form a mixture. Given that a 1.00-g sample of the mixture undergoes combustion to produce 1.20 g of CO_2 , what is the mass percentage of LSD in the mixture?

112. Methane (CH_4) is the main component of marsh gas. Heating methane in the presence of sulfur produces carbon disulfide and hydrogen sulfide as the only products.

Additional Exercises

103. Only one isotope of this element occurs in nature. One atom of this isotope has a mass of 9.123×10^{-23} g. Identify the element and give its atomic mass.

104. Many cereals are made with high moisture content so that the cereal can be formed into various shapes before it is dried. A cereal product containing 58% H_2O by mass is pro-

- a. Write the balanced chemical equation for the reaction of methane and sulfur.
- b. Calculate the theoretical yield of carbon disulfide when 120. g of methane is reacted with an equal mass of sulfur.
113. An iron ore sample contains Fe_2O_3 plus other impurities. A 752-g sample of impure iron ore is heated with excess carbon, producing 453 g of pure iron by the following reaction:



What is the mass percent of Fe_2O_3 in the impure iron ore sample? Assume that Fe_2O_3 is the only source of iron and that the reaction is 100% efficient.

114. Commercial brass, an alloy of Zn and Cu, reacts with hydrochloric acid as follows:

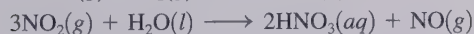
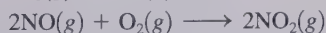
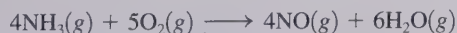


(Cu does not react with HCl.) When 0.5065 g of a certain brass alloy is reacted with excess HCl, 0.0985 g ZnCl_2 is eventually isolated.

- a. What is the composition of the brass by mass?
- b. How could this result be checked without changing the above procedure?
115. Vitamin A has a molar mass of 286.4 g/mol and a general molecular formula of $\text{C}_x\text{H}_y\text{E}$, where E is an unknown element. If vitamin A is 83.86% C and 10.56% H by mass, what is the molecular formula of vitamin A?

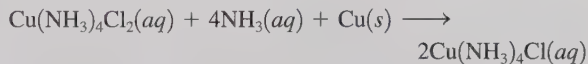
Challenge Problems

116. Natural rubidium has the average mass 85.4678 and is composed of isotopes ^{85}Rb (mass = 84.9117) and ^{87}Rb . The ratio of atoms $^{85}\text{Rb}/^{87}\text{Rb}$ in natural rubidium is 2.591. Calculate the mass of ^{87}Rb .
117. A compound contains only carbon, hydrogen, nitrogen, and oxygen. Combustion of 0.157 g of the compound produced 0.213 g CO_2 and 0.0310 g H_2O . In another experiment, it is found that 0.103 g of the compound produces 0.0230 g NH_3 . What is the empirical formula of the compound? *Hint:* Combustion involves reacting with excess O_2 . Assume that all the carbon ends up in CO_2 and all the hydrogen ends up in H_2O . Also assume that all the nitrogen ends up in the NH_3 in the second experiment.
118. Nitric acid is produced commercially by the Ostwald process, represented by the following equations:



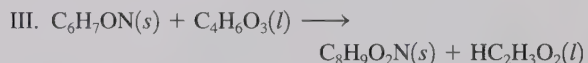
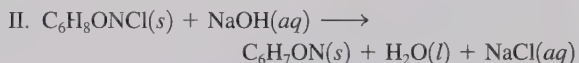
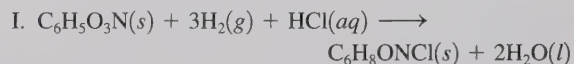
What mass of NH_3 must be used to produce 1.0×10^6 kg HNO_3 by the Ostwald process? Assume 100% yield in each reaction and assume that the NO produced in the third step is not recycled.

119. In the production of printed circuit boards for the electronics industry, a 0.60-mm layer of copper is laminated onto an insulating plastic board. Next, a circuit pattern made of a chemically resistant polymer is printed on the board. The unwanted copper is removed by chemical etching, and the protective polymer is finally removed by solvents. One etching reaction is



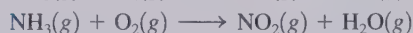
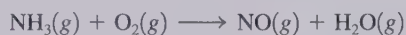
A plant needs to manufacture 10,000 printed circuit boards, each 8.0×16.0 cm in area. An average of 80.% of the copper is removed from each board (density of copper = 8.96 g/cm^3). What masses of $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ and NH_3 are needed to do this? Assume 100% yield.

120. The aspirin substitute, acetaminophen ($\text{C}_8\text{H}_9\text{O}_2\text{N}$), is produced by the following three-step synthesis:



The first two reactions have percent yields of 87% and 98% by mass, respectively. The overall reaction yields 3 mol of acetaminophen product for every 4 mol of $\text{C}_6\text{H}_5\text{O}_3\text{N}$ reacted.

- a. What is the percent yield by mass for the overall process?
- b. What is the percent yield by mass of step III?
121. An element X forms both a dichloride (XCl_2) and a tetrachloride (XCl_4). Treatment of 10.00 g XCl_2 with excess chlorine forms 12.55 g XCl_4 . Calculate the atomic mass of X, and identify X.
122. When $\text{M}_2\text{S}_3(s)$ is heated in air, it is converted to $\text{MO}_2(s)$. A 4.000-g sample of $\text{M}_2\text{S}_3(s)$ shows a decrease in mass of 0.277 g when it is heated in air. What is the average atomic mass of M?
123. When aluminum metal is heated with an element from Group 6A of the periodic table, an ionic compound forms. When the experiment is performed with an unknown Group 6A element, the product is 18.56% Al by mass. What is the formula of the compound?
124. A sample of a mixture containing only sodium chloride and potassium chloride has a mass of 4.000 g. When this sample is dissolved in water and excess silver nitrate is added, a white solid (silver chloride) forms. After filtration and drying, the solid silver chloride has the mass 8.5904 g. Calculate the mass percent of each mixture component.
125. Ammonia reacts with O_2 to form either $\text{NO}(g)$ or $\text{NO}_2(g)$ according to these unbalanced equations:



In a certain experiment 2.00 mol of $\text{NH}_3(\text{g})$ and 10.00 mol of $\text{O}_2(\text{g})$ are contained in a closed flask. After the reaction is complete, 6.75 mol of $\text{O}_2(\text{g})$ remains. Calculate the number of moles of $\text{NO}(\text{g})$ in the product mixture: (*Hint: You cannot do this problem by adding the balanced equations, because you cannot assume that the two reactions will occur with equal probability.*)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

126. From the information below, determine the mass of substance *C* that will be formed if 45.0 grams of substance *A* reacts with 23.0 grams of substance *B*. (Assume that the reaction between *A* and *B* goes to completion.)
- Substance *A* is a gray solid that consists of an alkaline earth metal and carbon (37.5% by mass). It reacts with substance *B* to produce substances *C* and *D*. Forty million trillion formula units of *A* have a mass of 4.26 milligrams.
 - 47.9 grams of substance *B* contains 5.36 grams of hydrogen and 42.5 grams of oxygen.
 - When 10.0 grams of *C* is burned in excess oxygen, 33.8 grams of carbon dioxide and 6.92 grams of water are produced. A mass spectrum of substance *C* shows a parent molecular ion with a mass-to-charge ratio of 26.
 - Substance *D* is the hydroxide of the metal in substance *A*.

Media Activities

- Open the Visualizations for Chapter 3 on the student CD to see two examples of very energetic chemical reactions.
 - In the oxygen and hydrogen video, H_2 by itself is not nearly as explosive as when a mixture of H_2 and O_2 is present. Why is this? (*Hint: Assume the sample containing only H_2 is reacting with O_2 in the surrounding air.*)
 - For the ammonium dichromate reaction, determine the balanced equation. Assume that ammonium dichromate is the only reactant and assume that chromium(III) oxide, nitrogen gas, and water vapor are the products. Check your answers by referencing Sample Exercise 3.14 in the text.

- Open the Conversation of Mass and Balancing Equations Understanding Concepts activity on the student CD to review important characteristics of chemical equations.
 - Try the Exercises to test your ability to balance chemical equations. Click on the + or – buttons to determine the correct coefficients. You must choose the coefficients for the reactants before determining the product coefficients. The best balanced equation has smallest whole number integers. However, any chemical equation can be balanced in an infinite number of ways. Explain.
 - Does the mole ratio between two species in a chemical equation change if smallest whole number integers are not used to balance the equation?
 - Using the Combustion of Methane Exercise, determine some combinations of coefficients other than smallest whole number integers to balance the equation. How are the coefficients related to the smallest whole number coefficients? Pick two substances and determine the mole ratio between these substances for each possible balanced reaction. How do the mole ratios compare?
- Open the Limiting Reactants Understanding Concepts activity on the student CD to examine limiting reactant problems on the microscopic level. The four exercises let you choose various numbers of reactant molecules, and then determine which is the limiting reactant. Consider the following combinations of reactant molecules that refer to the reactions in the Exercises.
 - If 2 molecules of acetylene are reacted with 4 molecules of oxygen, what is the limiting reactant? How many H_2O molecules can form? How many molecules of O_2 are required to react completely with 2 molecules of acetylene?
 - If 4 molecules of ammonia are reacted with 7 molecules of oxygen, what is the limiting reactant? How many NO molecules can form? How many O_2 molecules are required to react completely with 4 ammonia molecules?
 - If 2 molecules of hydrazine are reacted with 5 molecules of oxygen, what is the limiting reactant? How many H_2O molecules can form? How many O_2 molecules are required to react completely with 2 molecules of hydrazine?
 - If 3 molecules of methane are reacted with 5 molecules of oxygen, what is the limiting reactant? How many CO_2 molecules can form? How many molecules of O_2 are required to react completely with 3 molecules of methane?

Check your answers by answering the limiting reactant question and clicking the two Hint buttons.
- Test your understanding of Chapter 3 material by taking the ACE quizzes on the student web site.

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For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Types of Chemical Reactions and Solution Stoichiometry

Much of the chemistry that affects each of us occurs among substances dissolved in water. For example, virtually all the chemistry that makes life possible occurs in an aqueous environment. Also, various medical tests involve aqueous reactions, depending heavily on analyses of blood and other body fluids. In addition to the common tests for sugar, cholesterol, and iron, analyses for specific chemical markers allow detection of many diseases before obvious symptoms occur.

Aqueous chemistry is also important in our environment. In recent years, contamination of the groundwater by substances such as chloroform and nitrates has been widely publicized. Water is essential for life, and the maintenance of an ample supply of clean water is crucial to all civilization.

To understand the chemistry that occurs in such diverse places as the human body, the atmosphere, the groundwater, the oceans, the local water treatment plant, your hair as you shampoo it, and so on, we must understand how substances dissolved in water react with each other.

However, before we can understand solution reactions, we need to discuss the nature of solutions in which water is the dissolving medium, or *solvent*. These solutions are called **aqueous solutions**. In this chapter we will study the nature of materials after they are dissolved in water and various types of reactions that occur among these substances. You will see that the procedures developed in Chapter 3 to deal with chemical reactions work very well for reactions that take place in aqueous solutions. To understand the types of reactions that occur in aqueous solutions, we must first explore the types of species present. This requires an understanding of the nature of water.

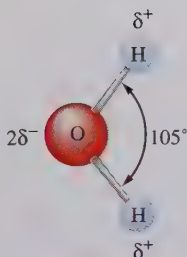
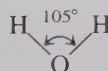
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4.1 Water, the Common Solvent

Water is one of the most important substances on earth. It is essential for sustaining the reactions that keep us alive, but it also affects our lives in many indirect ways. Water helps moderate the earth's temperature; it cools automobile engines, nuclear power plants, and many industrial processes; it provides a means of transportation on the earth's surface and a medium for the growth of a myriad of creatures we use as food; and much more.

One of the most valuable properties of water is its ability to dissolve many different substances. For example, salt “disappears” when you sprinkle it into the water used to cook vegetables, as does sugar when you add it to your iced tea. In each case the “disappearing” substance is obviously still present—you can taste it. What happens when a solid dissolves? To understand this process, we need to consider the nature of water. Liquid water consists of a collection of H_2O molecules. An individual H_2O molecule is “bent” or V-shaped, with an H—O—H angle of approximately 105 degrees:



The O—H bonds in the water molecule are covalent bonds formed by electron sharing between the oxygen and hydrogen atoms. However, the electrons of the bond are not shared equally between these atoms. For reasons we will discuss in later chapters, oxygen has a greater attraction for electrons than does hydrogen. If the electrons were shared equally between the two atoms, both would be electrically neutral because, on average, the number of electrons around each would equal the number of protons in that nucleus. However, because the oxygen atom has a greater attraction for electrons, the shared electrons tend to spend more time close to the oxygen than to either of the hydrogens. Thus the oxygen atom gains a slight excess of negative charge, and the hydrogen atoms become slightly positive. This is shown in Fig. 4.1, where δ (delta) indicates a *partial charge* (less than one unit of charge). Because of this unequal charge distribution, water is said to be a **polar molecule**. It is this polarity that gives water its great ability to dissolve compounds.

A schematic of an ionic solid dissolving in water is shown in Fig. 4.2. Note that the “positive ends” of the water molecules are attracted to the negatively charged anions and that the “negative ends” are attracted to the positively charged cations. This process is called **hydration**. The hydration of its ions tends to cause a salt to “fall apart” in the water, or to dissolve. The strong forces present among the positive and negative ions of the solid are replaced by strong water–ion interactions.

It is very important to recognize that when ionic substances (salts) dissolve in water, they break up into the *individual* cations and anions. For instance, when ammonium nitrate (NH_4NO_3) dissolves in water, the resulting solution contains NH_4^+ and NO_3^- ions moving around independently. This process can be represented as



where (aq) designates that the ions are hydrated by unspecified numbers of water molecules.

The **solubility** of ionic substances in water varies greatly. For example, sodium chloride is quite soluble in water, whereas silver chloride (contains Ag^+ and Cl^- ions) is only very slightly soluble. The differences in the solubilities of ionic compounds in water typically depend on the relative attractions of the ions for each other

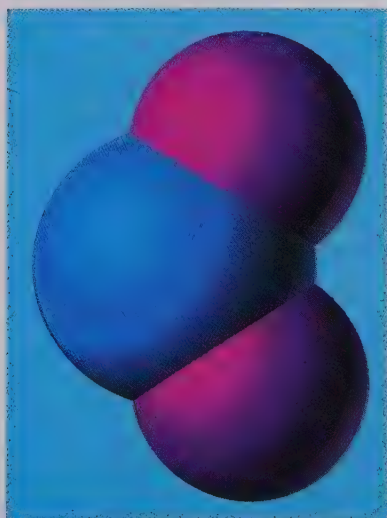
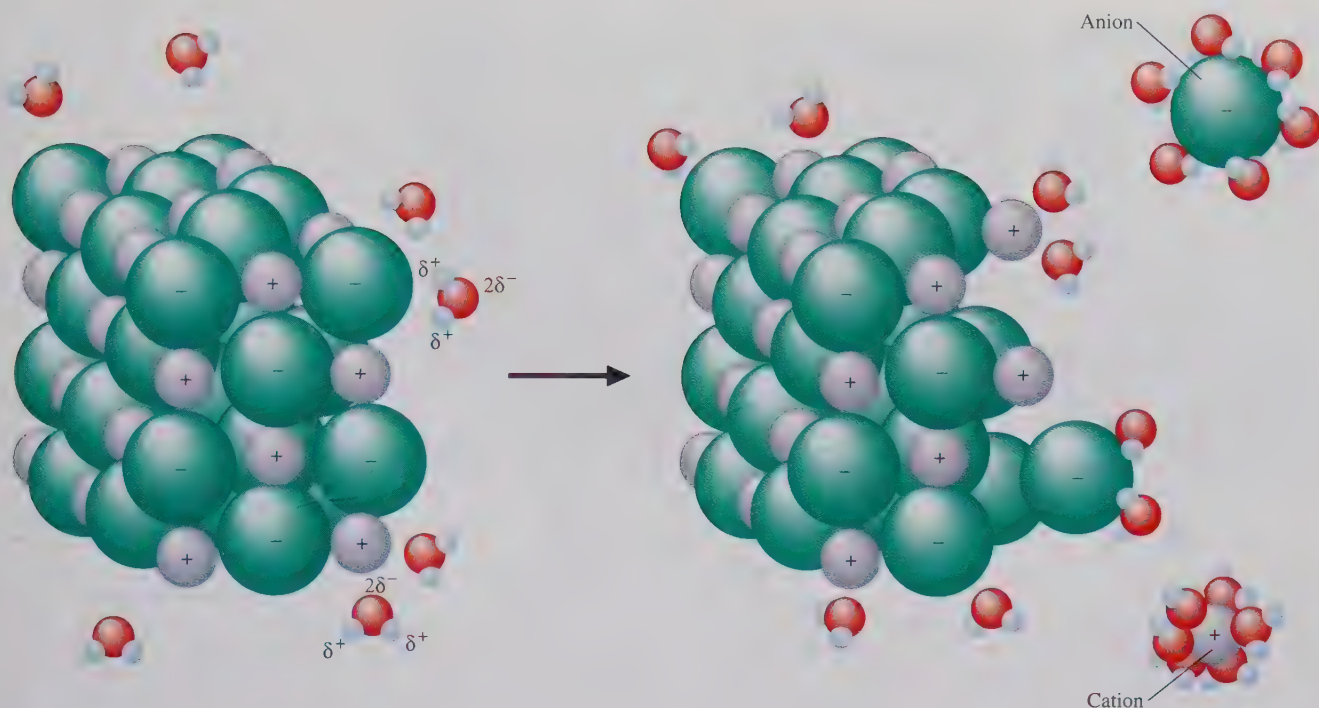


FIGURE 4.1
(top) The water molecule is polar.
(bottom) A space-filling model of the water molecule.

**FIGURE 4.2**

Polar water molecules interact with the positive and negative ions of a salt, assisting in the dissolving process.



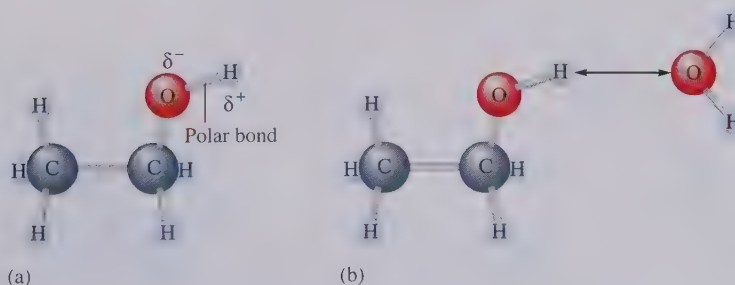
Visualization: The Dissolution of a Solid in a Liquid

(these forces hold the solid together) and the attractions of the ions for water molecules (which cause the solid to disperse [dissolve] in water). Solubility is a complex topic that we will explore in much more detail in Chapter 11. However, the most important thing to remember at this point is that when an ionic solid does dissolve in water, the ions become hydrated and are dispersed (move around independently).

Water also dissolves many nonionic substances. Ethanol ($\text{C}_2\text{H}_5\text{OH}$), for example, is very soluble in water. Wine, beer, and mixed drinks are aqueous solutions of ethanol and other substances. Why is ethanol so soluble in water? The answer lies in the structure of the alcohol molecules, which is shown in Fig. 4.3(a). The molecule contains a polar O—H bond like those in water, which makes it very compatible with water. The interaction of water with ethanol is represented in Fig. 4.3(b).

FIGURE 4.3

(a) The ethanol molecule contains a polar O—H bond similar to those in the water molecule. (b) The polar water molecule interacts strongly with the polar O—H bond in ethanol. This is a case of “like dissolving like.”



Many substances do not dissolve in water. Pure water will not, for example, dissolve animal fat, because fat molecules are nonpolar and do not interact effectively with polar water molecules. In general, polar and ionic substances are expected to be more soluble in water than nonpolar substances. “Like dissolves like” is a useful rule for predicting solubility. We will explore the basis for this generalization when we discuss the details of solution formation in Chapter 11.

4.2

The Nature of Aqueous Solutions: Strong and Weak Electrolytes

As we discussed in Chapter 2, a solution is a homogeneous mixture. It is the same throughout (the first sip of a cup of coffee is the same as the last), but its composition can be varied by changing the amount of dissolved substances (one can make weak or strong coffee). In this section we will consider what happens when a substance, the **solute**, is dissolved in liquid water, the **solvent**.

One useful property for characterizing a solution is its **electrical conductivity**, its ability to conduct an electric current. This characteristic can be checked conveniently by using an apparatus like the ones shown in Figure 4.4. If the solution in the container conducts electricity, the bulb lights. Pure water is not an electrical conductor. However, some aqueous solutions conduct current very efficiently, and the bulb shines very brightly; these solutions contain **strong electrolytes**. Other solutions conduct only a small current, and the bulb glows dimly; these solutions contain **weak electrolytes**. Some solutions permit no current to flow, and the bulb remains unlit; these solutions contain **nonelectrolytes**.

The basis for the conductivity properties of solutions was first correctly identified by Svante Arrhenius (1859–1927), then a Swedish graduate student in physics, who carried out research on the nature of solutions at the University of Uppsala in the early 1880s. Arrhenius came to believe that the conductivity of solutions arose from the presence of ions, an idea that was at first scorned by the majority of the scientific establishment. However, in the late 1890s when atoms were found to contain charged particles, the ionic theory suddenly made sense and became widely accepted.

As Arrhenius postulated, the extent to which a solution can conduct an electric current depends directly on the number of ions present. Some materials, such as sodium chloride, readily produce ions in aqueous solution and thus are strong electrolytes. Other substances, such as acetic acid, produce relatively few ions when dissolved in water and are weak electrolytes. A third class of materials, such as sugar, form virtually no ions when dissolved in water and are nonelectrolytes.

Strong Electrolytes

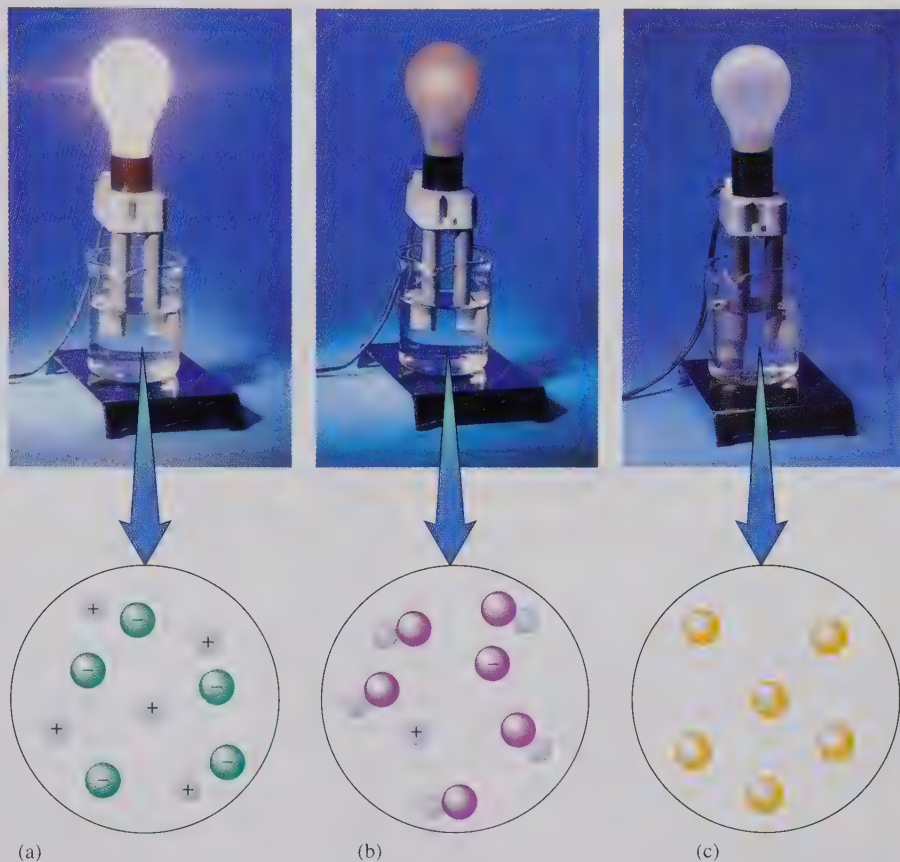
Strong electrolytes are substances that are completely ionized when they are dissolved in water, as represented in Fig. 4.4(a). We will consider several classes of strong electrolytes: (1) soluble salts, (2) strong acids, and (3) strong bases.

As shown in Fig. 4.2, a salt consists of an array of cations and anions that separate and become hydrated when the salt dissolves. For example, when NaCl dissolves in water, it produces hydrated Na^+ and Cl^- ions in the solution (see Fig. 4.5). Virtually no NaCl units are present. Thus NaCl is a strong electrolyte. It is important to recognize that these aqueous solutions contain millions of water molecules that we will not include in our molecular-level drawings.

An *electrolyte* is a substance that when dissolved in water produces a solution that can conduct electricity.

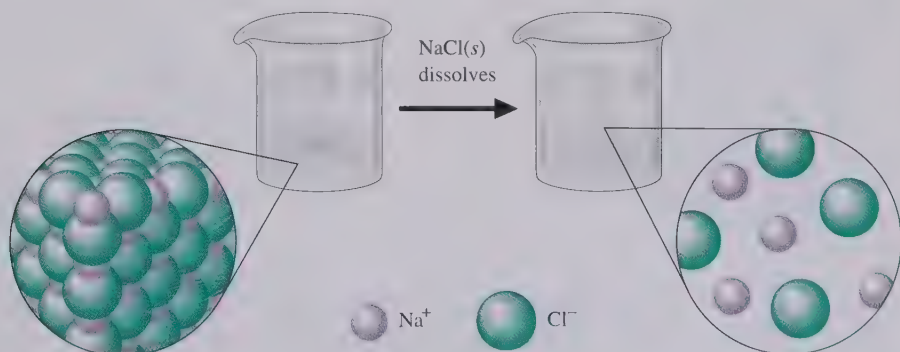
FIGURE 4.4

Electrical conductivity of aqueous solutions. The circuit will be completed and will allow current to flow only when there are charge carriers (ions) in the solution. *Note:* Water molecules are present but not shown in these pictures. (a) A hydrochloric acid solution, which is a strong electrolyte, contains ions that readily conduct the current and give a brightly lit bulb. (b) An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit. (c) A sucrose solution, which is a nonelectrolyte, contains no ions and does not conduct a current. The bulb remains unlit.



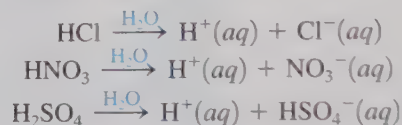
One of Arrhenius's most important discoveries concerned the nature of acids. Acidity was first associated with the sour taste of citrus fruits. In fact, the word *acid* comes directly from the Latin word *acidus*, meaning "sour." The mineral acids sulfuric acid (H_2SO_4) and nitric acid (HNO_3), so named because they were originally obtained by the treatment of minerals, were discovered around 1300.

Although acids were known for hundreds of years before the time of Arrhenius, no one had recognized their essential nature. In his studies of solutions, Arrhenius found that when the substances HCl , HNO_3 , and H_2SO_4 were dissolved in water,

**FIGURE 4.5**

When solid NaCl dissolves, the Na^+ and Cl^- ions are randomly dispersed in the water.

they behaved as strong electrolytes. He postulated that this was the result of ionization reactions in water, for example:



The Arrhenius definition of an acid is a substance that produces H^+ ions in solution.

Strong electrolytes dissociate (ionize) completely in aqueous solution.

Perchloric acid, $\text{HClO}_4(\text{aq})$, is another strong acid.

Thus Arrhenius proposed that an **acid** is a substance that produces H^+ ions (protons) when it is dissolved in water.

Studies of conductivity show that when HCl , HNO_3 , and H_2SO_4 are placed in water, *virtually every molecule ionizes*. These substances are strong electrolytes and are thus called **strong acids**. All three are very important chemicals, and much more will be said about them as we proceed. However, at this point the following facts are important:

Sulfuric acid, nitric acid, and hydrochloric acid are aqueous solutions and should be written in chemical equations as $\text{H}_2\text{SO}_4(\text{aq})$, $\text{HNO}_3(\text{aq})$, and $\text{HCl}(\text{aq})$, respectively, although they often appear without the (aq) symbol.

A strong acid is one that completely dissociates into its ions. Thus, if 100 molecules of HCl are dissolved in water, 100 H^+ ions and 100 Cl^- ions are produced. Virtually no HCl molecules exist in aqueous solutions (see Fig. 4.6).

Sulfuric acid is a special case. The formula H_2SO_4 indicates that this acid can produce two H^+ ions per molecule when dissolved in water. However, only the first H^+ ion is completely dissociated. The second H^+ ion can be pulled off under certain conditions, which we will discuss later. Thus an aqueous solution of H_2SO_4 contains mostly H^+ ions and HSO_4^- ions.

Another important class of strong electrolytes consists of the **strong bases**, soluble ionic compounds containing the hydroxide ion (OH^-). When these compounds are dissolved in water, the cations and OH^- ions separate and move independently. Solutions containing bases have a bitter taste and a slippery feel. The most common basic solutions are those produced when solid sodium hydroxide

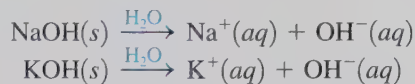


FIGURE 4.6
 $\text{HCl}(\text{aq})$ is completely ionized.



FIGURE 4.7
An aqueous solution of sodium hydroxide.

(NaOH) or potassium hydroxide (KOH) is dissolved in water to produce ions, as follows (see Fig. 4.7):



Weak Electrolytes

Weak electrolytes dissociate (ionize) only to a small extent in aqueous solution.

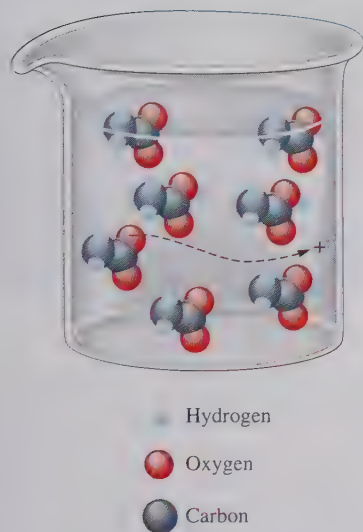
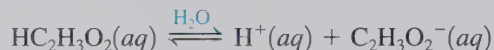


FIGURE 4.8

Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) exists in water mostly as undissociated molecules. Only a small percentage of the molecules are ionized.

Weak electrolytes are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water, as shown in Fig. 4.4(b). The most common weak electrolytes are weak acids and weak bases.

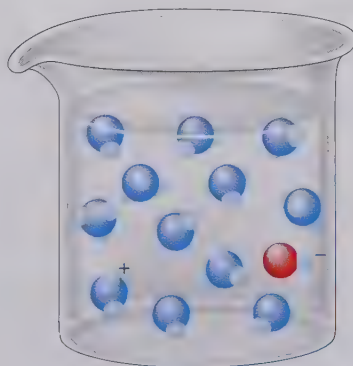
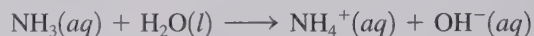
The main acidic component of vinegar is acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$). The formula is written to indicate that acetic acid has two chemically distinct types of hydrogen atoms. Formulas for acids are often written with the acidic hydrogen atom or atoms (any that will produce H^+ ions in solution) listed first. If any nonacidic hydrogens are present, they are written later in the formula. Thus the formula $\text{HC}_2\text{H}_3\text{O}_2$ indicates one acidic and three nonacidic hydrogen atoms. The dissociation reaction for acetic acid in water can be written as follows:



Acetic acid is very different from the strong acids because only about 1% of its molecules dissociate in aqueous solutions at typical concentrations. For example, in a solution containing 0.1 mole of $\text{HC}_2\text{H}_3\text{O}_2$ per liter, for every 100 molecules of $\text{HC}_2\text{H}_3\text{O}_2$ originally dissolved in water, approximately 99 molecules of $\text{HC}_2\text{H}_3\text{O}_2$ remain intact (see Fig. 4.8). That is, only one molecule out of every 100 dissociates (to produce one H^+ ion and one $\text{C}_2\text{H}_3\text{O}_2^-$ ion).

Because acetic acid is a weak electrolyte, it is called a **weak acid**. Any acid, such as acetic acid, that *dissociates (ionizes) only to a slight extent in aqueous solutions is called a weak acid*. In Chapter 14 we will explore the subject of weak acids in detail.

The most common weak base is ammonia (NH_3). When ammonia is dissolved in water, it reacts as follows:



The solution is *basic* because OH^- ions are produced. Ammonia is called a **weak base** because *the resulting solution is a weak electrolyte*; that is, very few ions are formed. In fact, in a solution containing 0.1 mole of NH_3 per liter, for every 100 molecules of NH_3 originally dissolved, only one NH_4^+ ion and one OH^- ion are produced; 99 molecules of NH_3 remain unreacted (see Fig. 4.9).

FIGURE 4.9

The reaction of NH_3 in water.

Arrhenius: A Man with Solutions

Science is a human endeavor, subject to human frailties and governed by personalities, politics, and prejudices. One of the best illustrations of the often bumpy path of the advancement of scientific knowledge is the story of Swedish chemist Svante Arrhenius.

When Arrhenius began studies toward his doctorate at the University of Uppsala around 1880, he chose to investigate the passage of electricity through solutions, a mystery that had baffled scientists for a century. The first experiments had been done in the 1770s by Cavendish, who compared the conductivity of salt solution with that of rain water using his own physiologic reaction to the electric shocks he received! Arrhenius had an array of instruments to measure electric current, but the process of carefully weighing, measuring, and recording data from a multitude of experiments was a tedious one.

After his long series of experiments was performed, Arrhenius quit his laboratory bench and returned to his coun-



Svante August Arrhenius.

Nonelectrolytes

Nonelectrolytes are substances that dissolve in water but do not produce any ions, as shown in Fig. 4.4(c). An example of a nonelectrolyte is ethanol (see Fig. 4.3 for the structural formula). When ethanol dissolves, entire C_2H_5OH molecules are dispersed in the water. Since the molecules do not break up into ions, the resulting solution does not conduct an electric current. Another common nonelectrolyte is table sugar (sucrose, $C_{12}H_{22}O_{11}$), which is very soluble in water but which produces no ions when it dissolves. The sucrose molecules remain intact.

4.3 The Composition of Solutions

Chemical reactions often take place when two solutions are mixed. To perform stoichiometric calculations in such cases, we must know two things: (1) the *nature of the reaction*, which depends on the exact forms the chemicals take when dissolved, and (2) the *amounts of chemicals* present in the solutions, usually expressed as concentrations.

The concentration of a solution can be described in many different ways, as we will see in Chapter 11. At this point we will consider only the most commonly used expression of concentration, **molarity** (M), which is defined as *moles of solute per volume of solution in liters*:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

A solution that is 1.0 molar (written as 1.0 M) contains 1.0 mole of solute per liter of solution.

try home to try to formulate a model that could account for his data. He wrote, "I got the idea in the night of the 17th of May in the year 1883, and I could not sleep that night until I had worked through the whole problem." His idea was that ions were responsible for conducting electricity through a solution.

Back at Uppsala, Arrhenius took his doctoral dissertation containing the new theory to his advisor, Professor Cleve, an eminent chemist and the discoverer of the elements holmium and thulium. Cleve's uninterested response was what Arrhenius had expected. It was in keeping with Cleve's resistance to new ideas—he had not even accepted Mendeleev's periodic table, introduced 10 years earlier.

It is a long-standing custom that before a doctoral degree is granted, the dissertation must be defended before a panel of professors. Although this procedure is still followed at most universities today, the problems are usually worked out in private with the evaluating professors before the actual defense. However, when Arrhenius did it, the dissertation defense was an open debate, which could be rancorous and humiliating. Knowing that it would be unwise to antagonize his professors, Arrhenius downplayed his convictions about his new theory as he defended his disser-

tation. His diplomacy paid off: He was awarded his degree, albeit reluctantly, because the professors still did not believe his model and considered him to be a marginal scientist, at best.

Such a setback could have ended his scientific career, but Arrhenius was a crusader; he was determined to see his theory triumph. He promptly embarked on a political campaign, enlisting the aid of several prominent scientists, to get his theory accepted.

Ultimately, the ionic theory triumphed. Arrhenius's fame spread, and honors were heaped on him, culminating in the Nobel Prize in chemistry in 1903. Not one to rest on his laurels, Arrhenius turned to new fields, including astronomy; he formulated a new theory that the solar system may have come into being through the collision of stars. His exceptional versatility led him to study the use of serums to fight disease, energy resources and conservation, and the origin of life.

Additional insight on Arrhenius and his scientific career can be obtained from his address on receiving the Willard Gibbs Award. See *Journal of the American Chemical Society* **36** (1912): 353.

SAMPLE EXERCISE 4.1

Calculation of Molarity I

Calculate the molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.

SOLUTION

To find the molarity of the solution, we first compute the number of moles of solute using the molar mass of NaOH (40.00 g/mol):

$$11.5 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.288 \text{ mol NaOH}$$

Then we divide by the volume of the solution in liters:

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.288 \text{ mol NaOH}}{1.50 \text{ L solution}} = 0.192 \text{ M NaOH}$$

See Exercises 4.15 and 4.16.

SAMPLE EXERCISE 4.2

Calculation of Molarity II

Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution.

SOLUTION

First we calculate the number of moles of HCl (molar mass = 36.46 g/mol):

$$1.56 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 4.28 \times 10^{-2} \text{ mol HCl}$$

Next we must change the volume of the solution to liters:

$$26.8 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.68 \times 10^{-2} \text{ L}$$

Finally, we divide the moles of solution by the liters of solution:

$$\text{Molarity} = \frac{4.28 \times 10^{-2} \text{ mol HCl}}{2.68 \times 10^{-2} \text{ L solution}} = 1.60 \text{ M HCl}$$

See Exercises 4.15 and 4.16.

It is important to realize that the conventional description of a solution's concentration may not accurately reflect the true composition of the solution. Solution concentration is always given in terms of the form of the solute *before* it dissolves. For example, when a solution is described as being 1.0 M NaCl, this means that the solution was prepared by dissolving 1.0 mole of solid NaCl in enough water to make 1.0 liter of solution; it does not mean that the solution contains 1.0 mole of NaCl units. Actually, the solution contains 1.0 mole of Na^+ ions and 1.0 mole of Cl^- ions. This situation is further illustrated in Sample Exercise 4.3.

SAMPLE EXERCISE 4.3

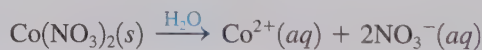
Concentrations of Ions I

Give the concentration of each type of ion in the following solutions:

- 0.50 M $\text{Co}(\text{NO}_3)_2$
- 1 M $\text{Fe}(\text{ClO}_4)_3$

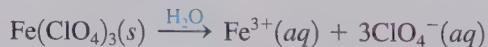
SOLUTION

- When solid $\text{Co}(\text{NO}_3)_2$ dissolves, the cobalt(II) cation and the nitrate anions separate:



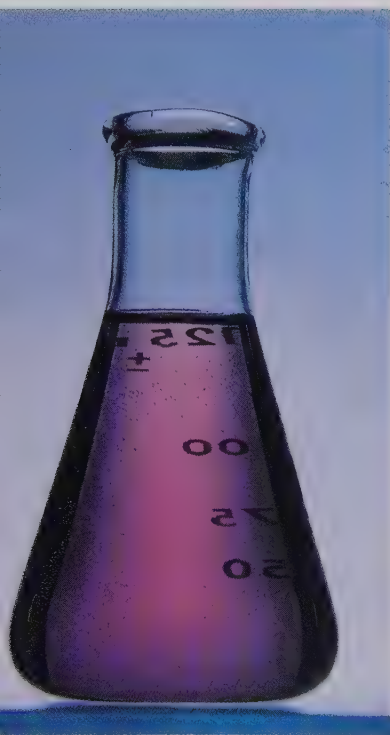
For each mole of $\text{Co}(\text{NO}_3)_2$ that is dissolved, the solution contains 1 mol Co^{2+} ions and 2 mol NO_3^- ions. Thus a solution that is 0.50 M $\text{Co}(\text{NO}_3)_2$ contains 0.50 M Co^{2+} and $(2 \times 0.50) \text{ M NO}_3^-$ or 1.0 M NO_3^- .

- When solid $\text{Fe}(\text{ClO}_4)_3$ dissolves, the iron(III) cation and the perchlorate anions separate:



Thus a solution that is described as 1 M $\text{Fe}(\text{ClO}_4)_3$ actually contains 1 M Fe^{3+} ions and 3 M ClO_4^- ions.

See Exercise 4.17.



An aqueous solution of $\text{Co}(\text{NO}_3)_2$.

Often chemists need to determine the number of moles of solute present in a given volume of a solution of known molarity. The procedure for doing this is easily derived from the definition of molarity. If we multiply the molarity of a solution by the volume (in liters) of a particular sample of the solution, we get the moles of solute present in that sample:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\begin{aligned} \text{Liters of solution} \times \text{molarity} &= \cancel{\text{liters of solution}} \times \frac{\text{moles of solute}}{\cancel{\text{liters of solution}}} \\ &= \text{moles of solute} \end{aligned}$$

This procedure is demonstrated in Sample Exercises 4.4 and 4.5.

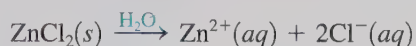
SAMPLE EXERCISE 4.4

Concentrations of Ions II

Calculate the number of moles of Cl^- ions in 1.75 L of $1.0 \times 10^{-3} M \text{ZnCl}_2$.

SOLUTION

When solid ZnCl_2 dissolves, it produces ions as follows:



Thus a $1.0 \times 10^{-3} M \text{ZnCl}_2$ solution contains $1.0 \times 10^{-3} M \text{Zn}^{2+}$ ions and $2.0 \times 10^{-3} M \text{Cl}^-$ ions. To calculate the moles of Cl^- ions in 1.75 L of the $1.0 \times 10^{-3} M \text{ZnCl}_2$ solution, we must multiply the volume times the molarity:

$$\begin{aligned} 1.75 \text{ L solution} \times 2.0 \times 10^{-3} M \text{Cl}^- &= 1.75 \cancel{\text{L solution}} \times \frac{2.0 \times 10^{-3} \text{ mol Cl}^-}{\cancel{\text{L solution}}} \\ &= 3.5 \times 10^{-3} \text{ mol Cl}^- \end{aligned}$$

See Exercise 4.19.

SAMPLE EXERCISE 4.5

Concentration and Volume

Typical blood serum is about $0.14 M \text{NaCl}$. What volume of blood contains 1.0 mg NaCl ?

SOLUTION

We must first determine the number of moles represented by 1.0 mg NaCl (molar mass = 58.45 g/mol):

$$1.0 \text{ mg NaCl} \times \frac{1 \cancel{\text{g NaCl}}}{1000 \cancel{\text{mg NaCl}}} \times \frac{1 \text{ mol NaCl}}{58.45 \cancel{\text{g NaCl}}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

Next, we must determine what volume of $0.14 M \text{NaCl}$ solution contains $1.7 \times 10^{-5} \text{ mol NaCl}$. There is some volume, call it V , that when multiplied by the molarity of this solution will yield $1.7 \times 10^{-5} \text{ mol NaCl}$, that is:

$$V \times \frac{0.14 \text{ mol NaCl}}{\text{L solution}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

We want to solve for the volume:

$$V = \frac{1.7 \times 10^{-5} \cancel{\text{mol NaCl}}}{\frac{0.14 \cancel{\text{mol NaCl}}}{\text{L solution}}} = 1.2 \times 10^{-4} \text{ L solution}$$

Thus 0.12 mL of blood contains $1.7 \times 10^{-5} \text{ mol NaCl}$ or 1.0 mg NaCl .

See Exercises 4.21 and 4.22.

A **standard solution** is a *solution whose concentration is accurately known*. Standard solutions, often used in chemical analysis, can be prepared as shown in Fig. 4.10 and in Sample Exercise 4.6.

SAMPLE EXERCISE 4.6

Solutions of Known Concentration

To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate) solution. How much solid $\text{K}_2\text{Cr}_2\text{O}_7$ must be weighed out to make this solution?

SOLUTION

We must first determine the moles of $\text{K}_2\text{Cr}_2\text{O}_7$ required:

$$1.00 \text{ L solution} \times \frac{0.200 \text{ mol K}_2\text{Cr}_2\text{O}_7}{\text{L solution}} = 0.200 \text{ mol K}_2\text{Cr}_2\text{O}_7$$

This amount can be converted to grams using the molar mass of $\text{K}_2\text{Cr}_2\text{O}_7$ (294.18 g/mol).

$$0.200 \text{ mol K}_2\text{Cr}_2\text{O}_7 \times \frac{294.20 \text{ g K}_2\text{Cr}_2\text{O}_7}{\text{mol K}_2\text{Cr}_2\text{O}_7} = 58.8 \text{ g K}_2\text{Cr}_2\text{O}_7$$

Thus, to make 1.00 L of 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$, the chemist must weigh out 58.8 g $\text{K}_2\text{Cr}_2\text{O}_7$, transfer it to a 1.00-L volumetric flask, and add distilled water to the mark on the flask.

See Exercises 4.23a and c and 4.24c and e.

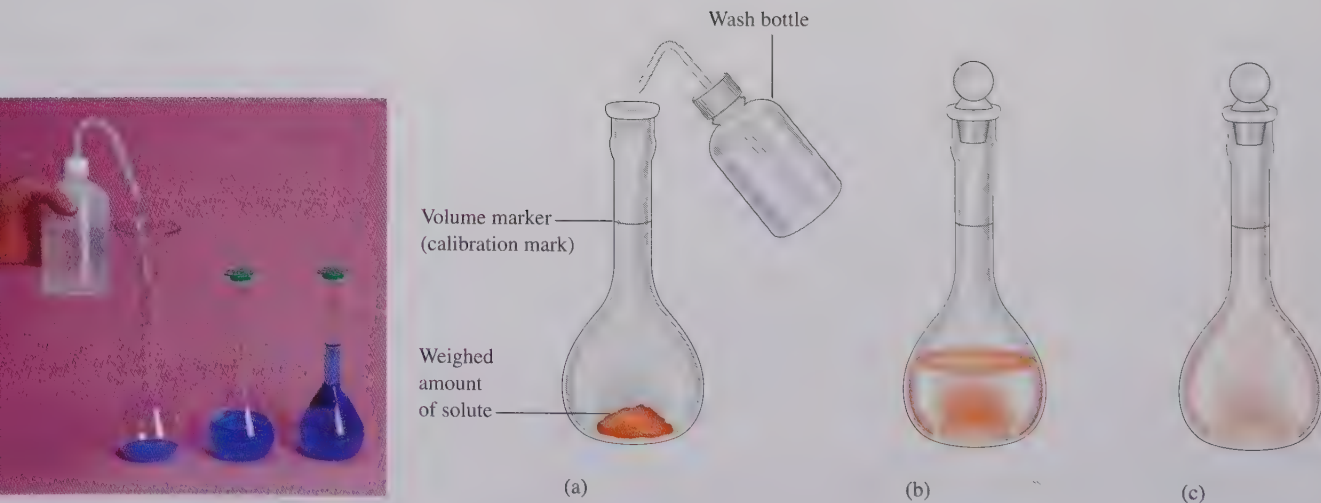


FIGURE 4.10

Steps involved in the preparation of a standard aqueous solution. (a) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water. (b) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (c) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. Then mix the solution thoroughly by inverting the flask several times.

Dilution

To save time and space in the laboratory, routinely used solutions are often purchased or prepared in concentrated form (called *stock solutions*). Water is then added to achieve the molarity desired for a particular solution. This process is called **dilution**. For example, the common acids are purchased as concentrated solutions and diluted as needed. A typical dilution calculation involves determining how much water must be added to an amount of stock solution to achieve a solution of the desired concentration. The key to doing these calculations is to remember that

$$\text{Moles of solute after dilution} = \text{moles of solute before dilution}$$

because only water (no solute) is added to accomplish the dilution.

For example, suppose we need to prepare 500. mL of 1.00 *M* acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) from a 17.4 *M* stock solution of acetic acid. What volume of the stock solution is required? The first step is to determine the number of moles of acetic acid in the final solution by multiplying the volume by the molarity (remembering that the volume must be changed to liters):

$$500. \text{ mL solution} \times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} \times \frac{1.00 \text{ mol HC}_2\text{H}_3\text{O}_2}{\text{L solution}} = 0.500 \text{ mol HC}_2\text{H}_3\text{O}_2$$

Thus we need to use a volume of 17.4 *M* acetic acid that contains 0.500 mol $\text{HC}_2\text{H}_3\text{O}_2$. That is,

$$V \times \frac{17.4 \text{ mol HC}_2\text{H}_3\text{O}_2}{\text{L solution}} = 0.500 \text{ mol HC}_2\text{H}_3\text{O}_2$$

Solving for *V* gives

$$V = \frac{0.500 \text{ mol HC}_2\text{H}_3\text{O}_2}{17.4 \text{ mol HC}_2\text{H}_3\text{O}_2 / \text{L solution}} = 0.0287 \text{ L or } 28.7 \text{ mL solution}$$

Thus, to make 500 mL of a 1.00 *M* acetic acid solution, we can take 28.7 mL of 17.4 *M* acetic acid and dilute it to a total volume of 500 mL with distilled water.

A dilution procedure typically involves two types of glassware: a pipet and a volumetric flask. A *pipet* is a device for accurately measuring and transferring a given volume of solution. There are two common types of pipets: *volumetric* (or *transfer*) *pipets* and *measuring pipets*, as shown in Fig. 4.11. Volumetric pipets come in specific sizes, such as 5 mL, 10 mL, 25 mL, and so on. Measuring pipets are used to measure volumes for which a volumetric pipet is not available. For example, we would use a measuring pipet as shown in Fig. 4.12 to deliver 28.7 mL of 17.4 *M* acetic acid into a 500-mL volumetric flask and then add water to the mark to perform the dilution described above.

Dilution with water does not alter the numbers of moles of solute present.

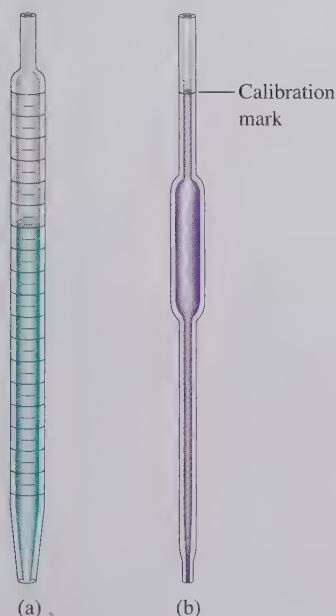


FIGURE 4.11

(a) A measuring pipet is graduated and can be used to measure various volumes of liquid accurately. (b) A volumetric (transfer) pipet is designed to measure one volume accurately. When filled to the mark, it delivers the volume indicated on the pipet.

SAMPLE EXERCISE 4.7

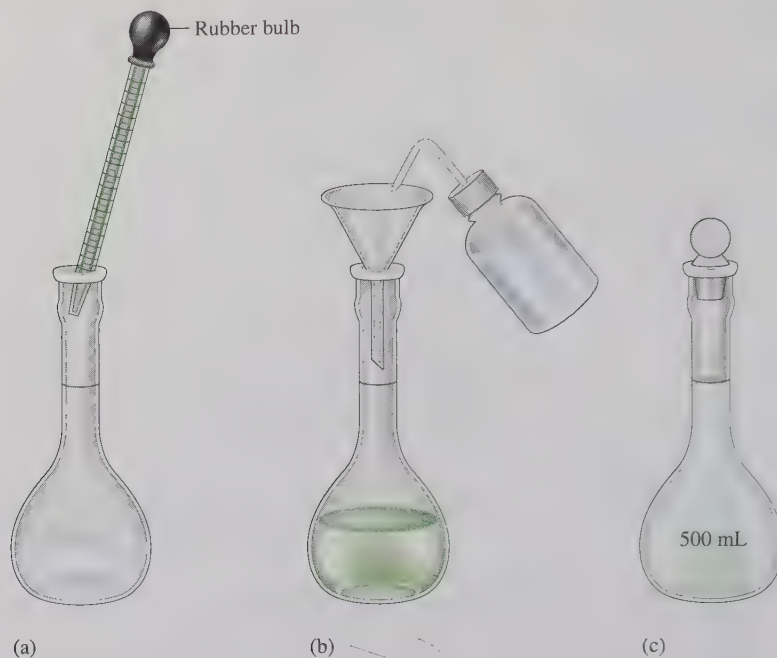
Concentration and Volume

What volume of 16 *M* sulfuric acid must be used to prepare 1.5 L of a 0.10 *M* H_2SO_4 solution?

SOLUTION

We must first determine the moles of H_2SO_4 in 1.5 L of 0.10 *M* H_2SO_4 :

$$1.5 \text{ L solution} \times \frac{0.10 \text{ mol H}_2\text{SO}_4}{\text{L solution}} = 0.15 \text{ mol H}_2\text{SO}_4$$

**FIGURE 4.12**

(a) A measuring pipet is used to transfer 28.7 mL of 17.4 *M* acetic acid solution to a volumetric flask. (b) Water is added to the flask to the calibration mark. (c) The resulting solution is 1.00 *M* acetic acid.

Next we must find the volume of 16 *M* H₂SO₄ that contains 0.15 mol H₂SO₄:

$$V \times \frac{16 \text{ mol H}_2\text{SO}_4}{\text{L solution}} = 0.15 \text{ mol H}_2\text{SO}_4$$

Solving for *V* gives

$$V = \frac{0.15 \text{ mol H}_2\text{SO}_4}{\frac{16 \text{ mol H}_2\text{SO}_4}{1 \text{ L solution}}} = 9.4 \times 10^{-3} \text{ L or } 9.4 \text{ mL solution}$$

In diluting an acid, "Do what you oughta,
always add acid to water."

Thus, to make 1.5 L of 0.10 *M* H₂SO₄ using 16 *M* H₂SO₄, we must take 9.4 mL of the concentrated acid and dilute it with water to 1.5 L. The correct way to do this is to add the 9.4 mL of acid to about 1 L of distilled water and then dilute to 1.5 L by adding more water.

See Exercises 4.23b and d and 4.24a, b, and d.

As noted earlier, the central idea in performing the calculations associated with dilutions is to recognize that the moles of solute are not changed by the dilution. Another way to express this condition is by the following equation:

$$M_1V_1 = M_2V_2$$

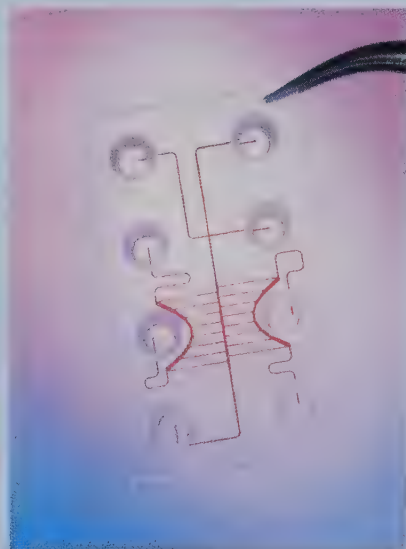
Tiny Laboratories

One of the major impacts of modern technology is to make things smaller. The best example is the computer. Calculations that 30 years ago required a machine the size of a large room now can be carried out on a hand-held calculator. This tendency toward miniaturization is also having a major impact on the science of chemical analysis. Using the techniques of computer chip makers, researchers are now constructing minuscule laboratories on the surface of a tiny chip made of silicon, glass, or plastic (see photo). Instead of electrons, 10^{-6} to 10^{-9} L of liquids move between reaction chambers on the chip through tiny capillaries. The chips typically contain no moving parts. Instead of conventional pumps, the chip-based laboratories use voltage differences to move liquids that contain ions from one reaction chamber to another.

Microchip laboratories have many advantages. They require only tiny amounts of sample. This is especially advantageous for expensive, difficult-to-prepare materials or in cases such as criminal investigations, where only small amounts of evidence may exist. The chip laboratories also minimize contamination because they represent a “closed system” once the material has been introduced to the chip. In addition, the chips can be made to be disposable to prevent cross-contamination of different samples.

The chip laboratories present some difficulties not found in macroscopic laboratories. The main problem concerns the large surface area of the capillaries and reaction chambers relative to the sample volume. Molecules or biological cells in the sample solution encounter so much “wall” that they may undergo unwanted reactions with the wall materials. Glass seems to present the least of these problems, and the walls of silicon chip laboratories can be protected by formation of relatively inert silicon dioxide. Because plastic is inexpensive, it seems a good choice for disposable chips, but plastic also is the most reactive with the samples and the least durable of the available materials.

Caliper Technologies Corporation, of Palo Alto, California, is working toward creating a miniature chemistry laboratory about the size of a toaster that can be used with “plug-in” chip-based laboratories. Various chips would be furnished with the unit that would be appropriate for different types of analyses. The entire unit would be connected to a computer to collect and analyze the data. There is even the possibility that these “laboratories” could be used in the home to perform analyses such as blood sugar and blood cholesterol and to check for the presence of bacteria such as *E. coli* and many others. This would revolutionize the health care industry.



Plastic chips such as this one made by Caliper Technologies are being used to perform laboratory procedures traditionally done with test tubes.

Adapted from “The Incredible Shrinking Laboratory,” by Corinna Wu, as appeared in *Science News*, Vol. 154, August 15, 1998, p. 104.

where M_1 and V_1 represent the molarity and volume of the original solution (before dilution) and M_2 and V_2 represent the molarity and volume of the diluted solution. This equation makes sense because

$$\begin{aligned} M_1 \times V_1 &= \text{mol solute before dilution} \\ &= \text{mol solute after dilution} = M_2 \times V_2 \end{aligned}$$

Repeat Sample Exercise 4.7 using the equation $M_1V_1 = M_2V_2$. Note that in doing so

$$M_1 = 16\text{ M} \quad M_2 = 0.10\text{ M} \quad V_2 = 1.5\text{ L}$$

and V_1 is the unknown quantity sought. The equation $M_1V_1 = M_2V_2$ always holds for a dilution. This equation will be easy for you to remember if you understand where it comes from.

4.4 Types of Chemical Reactions

Although we have considered many reactions so far in this text, we have examined only a tiny fraction of the millions of possible chemical reactions. To make sense of all these reactions, we need some system for grouping reactions into classes. Although there are many different ways to do this, we will use the system most commonly used by practicing chemists:

Types of Solution Reactions

- Precipitation reactions
- Acid–base reactions
- Oxidation–reduction reactions

Virtually all reactions can be put into one of these classes. We will define and illustrate each type in the following sections.

4.5 Precipitation Reactions

When two solutions are mixed, an insoluble substance sometimes forms; that is, a solid forms and separates from the solution. Such a reaction is called a **precipitation reaction**, and the solid that forms is called a **precipitate**. For example, a precipitation reaction occurs when an aqueous solution of potassium chromate, $\text{K}_2\text{CrO}_4(aq)$, which is yellow, is added to a colorless aqueous solution containing barium nitrate, $\text{Ba}(\text{NO}_3)_2(aq)$. As shown in Fig. 4.13, when these solutions are mixed, a yellow solid forms. What is the equation that describes this chemical change? To write the equation, we must know the identities of the reactants and products. The reactants have already been described: $\text{K}_2\text{CrO}_4(aq)$ and $\text{Ba}(\text{NO}_3)_2(aq)$. Is there some way we can predict the identities of the products? In particular, what is the yellow solid?

The best way to predict the identity of this solid is to think carefully about what products are possible. To do this, we need to know what species are present in the

A precipitation reaction also can be called a double displacement reaction.



Understanding Concepts:
Precipitation Reactions

The quantitative aspects of precipitation reactions are covered in Chapter 15.

When ionic compounds dissolve in water, the resulting solution contains the separated ions.

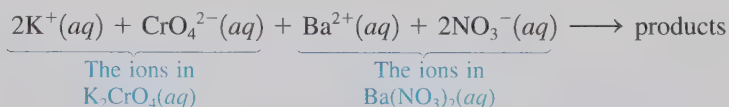
solution after the two reactant solutions are mixed. First, let's think about the nature of each reactant solution. The designation $\text{Ba}(\text{NO}_3)_2(\text{aq})$ means that barium nitrate (a white solid) has been dissolved in water. Notice that barium nitrate contains the Ba^{2+} and NO_3^- ions. *Remember: In virtually every case, when a solid containing ions dissolves in water, the ions separate and move around independently.* That is, $\text{Ba}(\text{NO}_3)_2(\text{aq})$ does not contain $\text{Ba}(\text{NO}_3)_2$ units; it contains separated Ba^{2+} and NO_3^- ions. See Fig. 4.14(a).

Similarly, since solid potassium chromate contains the K^+ and CrO_4^{2-} ions, an aqueous solution of potassium chromate (which is prepared by dissolving solid K_2CrO_4 in water) contains these separated ions, as shown in Fig. 4.14(b).

We can represent the mixing of $\text{K}_2\text{CrO}_4(\text{aq})$ and $\text{Ba}(\text{NO}_3)_2(\text{aq})$ in two ways. First, we can write



However, a much more accurate representation is



Thus the mixed solution contains the ions:



as illustrated in Fig. 4.15(a).

How can some or all of these ions combine to form a yellow solid? This is not an easy question to answer. In fact, predicting the products of a chemical reaction is one of the hardest things a beginning chemistry student is asked to do. Even an



FIGURE 4.13

When yellow aqueous potassium chromate is added to a colorless barium nitrate solution, yellow barium chromate precipitates.

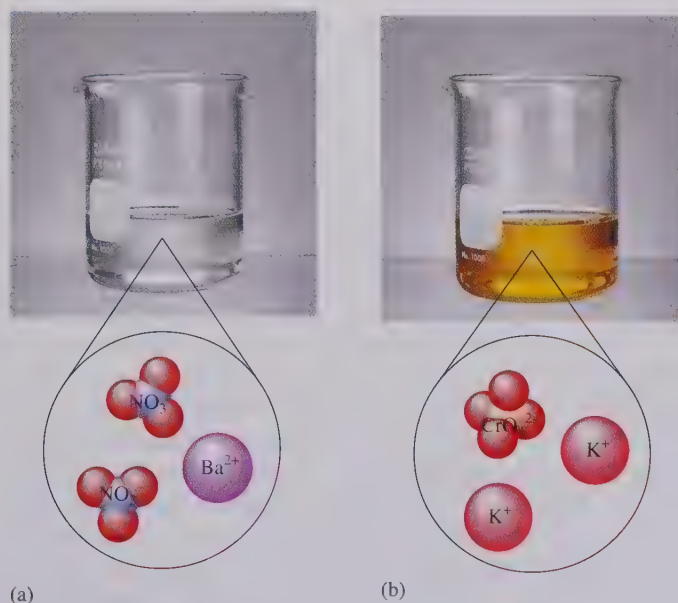
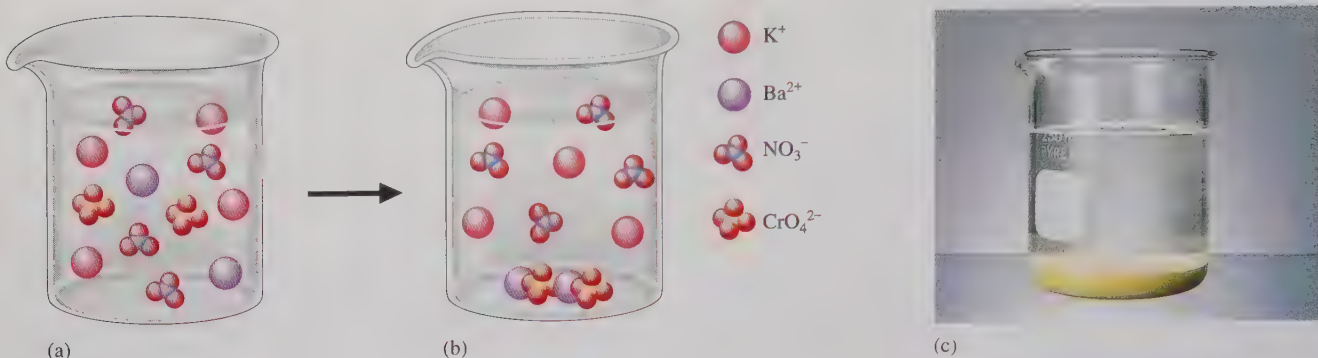


FIGURE 4.14

Reactant solutions: (a) $\text{Ba}(\text{NO}_3)_2(\text{aq})$ and (b) $\text{K}_2\text{CrO}_4(\text{aq})$

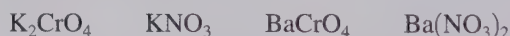
**FIGURE 4.15**

The reaction of $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$. (a) The molecular-level “picture” of the mixed solution before any reaction has occurred. (b) The molecular-level “picture” of the solution after the reaction has occurred to form $BaCrO_4(s)$. (c) A photo of the solution after the reaction has occurred, showing the solid $BaCrO_4$ on the bottom.

experienced chemist, when confronted with a new reaction, is often not sure what will happen. The chemist tries to think of the various possibilities, considers the likelihood of each possibility, and then makes a prediction (an educated guess). Only after identifying each product *experimentally* is the chemist sure what reaction has taken place. However, an educated guess is very useful because it provides a place to start. It tells us what kinds of products we are most likely to find. We already know some things that will help us predict the products of the above reaction.

1. When ions form a solid compound, the compound must have a zero net charge. Thus the products of this reaction must contain *both anions and cations*. For example, K^+ and Ba^{2+} could not combine to form the solid, nor could CrO_4^{2-} and NO_3^- .
2. Most ionic materials contain only two types of ions: one type of cation and one type of anion (for example, $NaCl$, KOH , Na_2SO_4 , K_2CrO_4 , $Co(NO_3)_2$, NH_4Cl , Na_2CO_3).

The possible combinations of a given cation and a given anion from the list of ions K^+ , CrO_4^{2-} , Ba^{2+} , and NO_3^- are

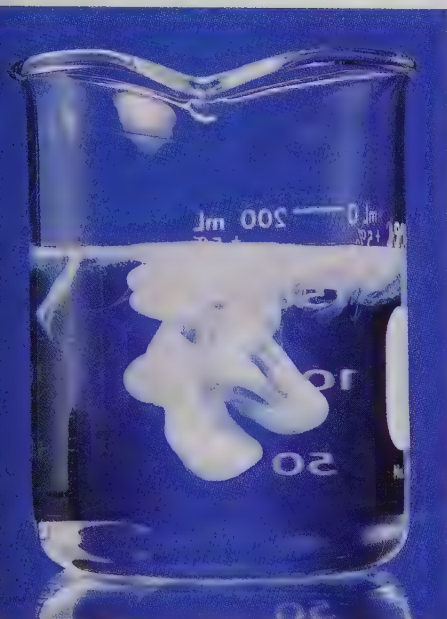


Which of these possibilities is most likely to represent the yellow solid? We know it's not K_2CrO_4 or $Ba(NO_3)_2$. They are the reactants. They were present (dissolved) in the separate solutions that were mixed. The only real possibilities for the solid that formed are



To decide which of these most likely represents the yellow solid, we need more facts. An experienced chemist knows that the K^+ ion and the NO_3^- ion are both colorless. Thus, if the solid is KNO_3 , it should be white, not yellow. On the other hand, the CrO_4^{2-} ion is yellow (note in Fig. 4.14 that $K_2CrO_4(aq)$ is yellow). Thus the yellow solid is almost certainly $BaCrO_4$. Further tests show that this is the case.

So far we have determined that one product of the reaction between $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$ is $BaCrO_4(s)$, but what happened to the K^+ and NO_3^- ions? The answer is that these ions are left dissolved in the solution; KNO_3 does not form a solid when the K^+ and NO_3^- ions are present in this much water. In other words, if we took solid KNO_3 and put it in the same quantity of water as is present in the mixed solution, it would dissolve. Thus, when we mix $K_2CrO_4(aq)$ and

**FIGURE 4.16**

Precipitation of silver chloride by mixing solutions of silver nitrate and potassium chloride. The K^+ and NO_3^- ions remain in solution.

$\text{Ba}(\text{NO}_3)_2(aq)$, $\text{BaCrO}_4(s)$ forms, but KNO_3 is left behind in solution (we write it as $\text{KNO}_3(aq)$). Thus the equation for this precipitation reaction is

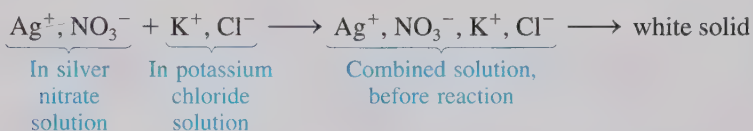


As long as water is present, the KNO_3 remains dissolved. (See Fig. 4.15 to help visualize what is happening in this reaction. Note the solid BaCrO_4 on the bottom of the container, while the K^+ and NO_3^- ions remain dispersed in the solution.) If we removed the solid BaCrO_4 and then evaporated the water, white solid KNO_3 would be obtained; the K^+ and NO_3^- ions assemble themselves into solid KNO_3 when the water is removed.

Now let's consider another example. When an aqueous solution of silver nitrate is added to an aqueous solution of potassium chloride, a white precipitate forms, as shown in Fig. 4.16. We can represent what we know so far as



Remembering that when ionic substances dissolve in water, the ions separate, we can write



Since we know the white solid must contain both positive and negative ions, the possible compounds that can be assembled from this collection of ions are



Since AgNO_3 and KCl are the substances dissolved in the two reactant solutions, we know that they do not represent the white solid product. Therefore, the only real possibilities are



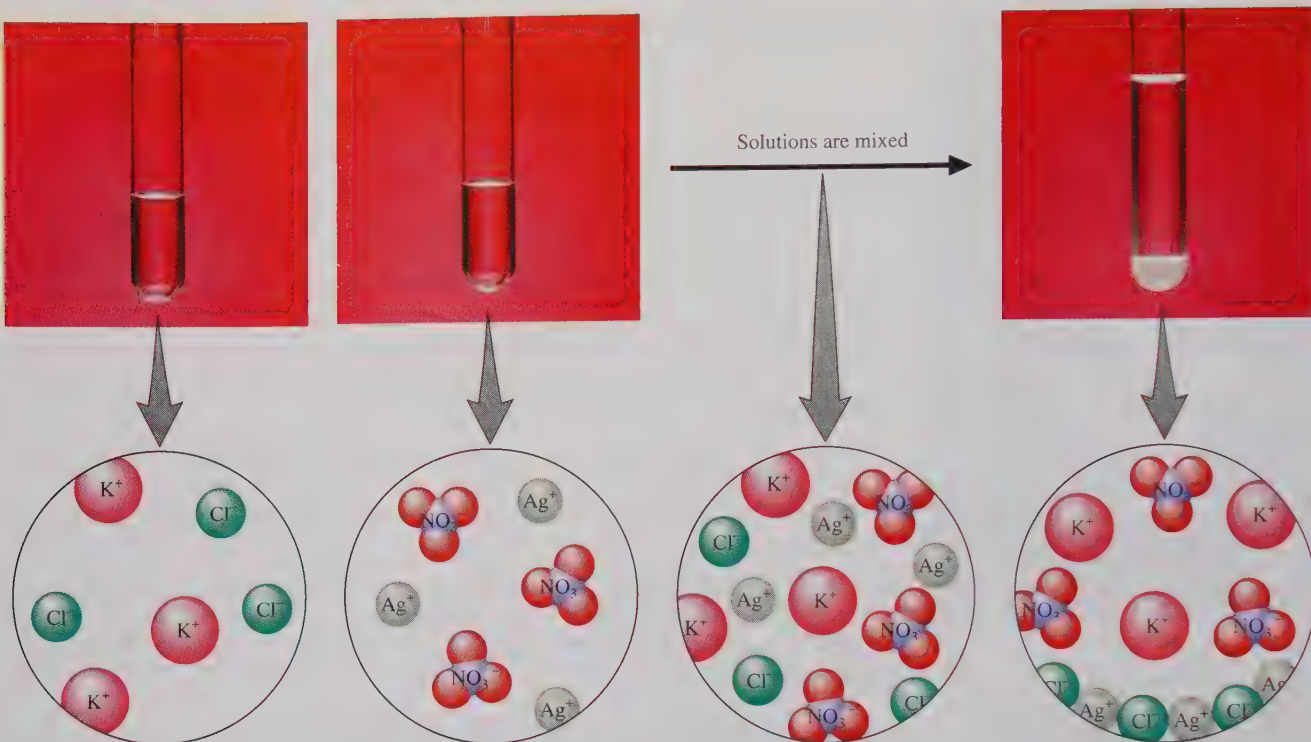
From the first example considered, we know that KNO_3 is quite soluble in water. Thus solid KNO_3 will not form when the reactant solids are mixed. The product must be $\text{AgCl}(s)$ (which can be proved by experiment to be true). The equation for the reaction now can be written



Figure 4.17 shows the result of mixing aqueous solutions of AgNO_3 and KCl , including a microscopic visualization of the reaction.

Notice that in these two examples we had to apply both concepts (solids must have a zero net charge) and facts (KNO_3 is very soluble in water, CrO_4^{2-} is yellow, and so on). Doing chemistry requires both understanding ideas and remembering key information. Predicting the identity of the solid product in a precipitation reaction requires knowledge of the solubilities of common ionic substances. As an aid in predicting the products of precipitation reactions, some simple solubility rules are given in Table 4.1. You should memorize these rules.

The phrase *slightly soluble* used in the solubility rules in Table 4.1 means that the tiny amount of solid that dissolves is not noticeable. The solid appears to be insoluble to the naked eye. Thus the terms *insoluble* and *slightly soluble* are often used interchangeably.

**FIGURE 4.17**

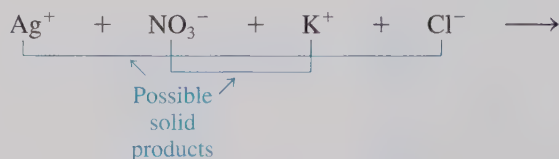
Photos and accompanying molecular-level representations illustrating the reaction of KCl(aq) with AgNO₃(aq) to form AgCl(s). Note that it is not possible to have a photo of the mixed solution before the reaction occurs, because it is an imaginary step that we use to help visualize the reaction. Actually, the reaction occurs immediately when the two solutions are mixed.

TABLE 4.1 Simple Rules for the Solubility of Salts in Water

1. Most nitrate (NO₃⁻) salts are soluble.
2. Most salts containing the alkali metal ions (Li⁺, Na⁺, K⁺, Cs⁺, Rb⁺) and the ammonium ion (NH₄⁺) are soluble.
3. Most chloride, bromide, and iodide salts are soluble. Notable exceptions are salts containing the ions Ag⁺, Pb²⁺, and Hg₂²⁺.
4. Most sulfate salts are soluble. Notable exceptions are BaSO₄, PbSO₄, Hg₂SO₄, and CaSO₄.
5. Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds Ba(OH)₂, Sr(OH)₂, and Ca(OH)₂ are marginally soluble.
6. Most sulfide (S²⁻), carbonate (CO₃²⁻), chromate (CrO₄²⁻), and phosphate (PO₄³⁻) salts are only slightly soluble.

Note that the information in Table 4.1 allows us to predict that AgCl is the white solid formed when solutions of AgNO_3 and KCl are mixed. Rules 1 and 2 indicate that KNO_3 is soluble, and Rule 3 states that AgCl is insoluble.

When solutions containing ionic substances are mixed, it will be helpful in determining the products if you think in terms of *ion interchange*. For example, in the preceding discussion we considered the results of mixing $\text{AgNO}_3(aq)$ and $\text{KCl}(aq)$. In determining the products, we took the cation from one reactant and combined it with the anion of the other reactant:



The solubility rules in Table 4.1 allow us to predict whether either product forms as a solid.

The key to dealing with the chemistry of an aqueous solution is first to *focus on the actual components of the solution before any reaction occurs* and then to figure out how these components will react with each other. Sample Exercise 4.8 illustrates this process for three different reactions.

To begin, focus on the ions in solution before any reaction occurs.

SAMPLE EXERCISE 4.8

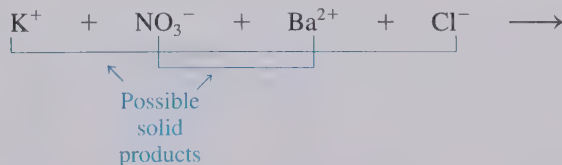
Predicting Reaction Products

Using the solubility rules in Table 4.1, predict what will happen when the following pairs of solutions are mixed.

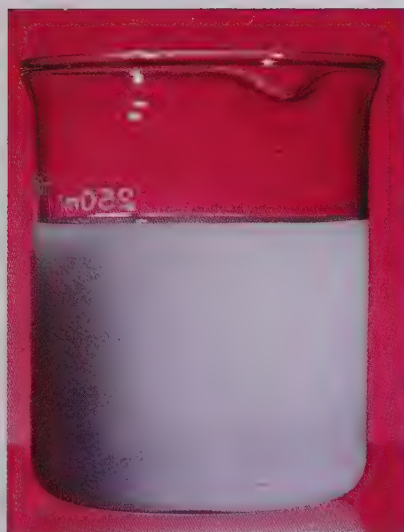
- $\text{KNO}_3(aq)$ and $\text{BaCl}_2(aq)$
- $\text{Na}_2\text{SO}_4(aq)$ and $\text{Pb}(\text{NO}_3)_2(aq)$
- $\text{KOH}(aq)$ and $\text{Fe}(\text{NO}_3)_3(aq)$

SOLUTION

- a. $\text{KNO}_3(aq)$ is an aqueous solution obtained by dissolving solid KNO_3 in water to form a solution containing the hydrated ions $\text{K}^+(aq)$ and $\text{NO}_3^-(aq)$. Likewise, $\text{BaCl}_2(aq)$ is a solution formed by dissolving solid BaCl_2 in water to produce $\text{Ba}^{2+}(aq)$ and $\text{Cl}^-(aq)$. When these two solutions are mixed, the resulting solution contains the ions K^+ , NO_3^- , Ba^{2+} , and Cl^- . All ions are hydrated, but the (aq) is omitted for simplicity. To look for possible solid products, combine the cation from one reactant with the anion from the other:



Note from Table 4.1 that the rules predict that both KCl and $\text{Ba}(\text{NO}_3)_2$ are soluble in water. Thus no precipitate forms when $\text{KNO}_3(aq)$ and $\text{BaCl}_2(aq)$ are mixed. All the ions remain dissolved in solution. No chemical reaction occurs.

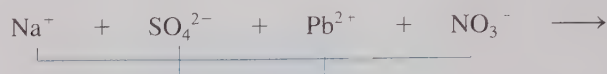


Lead sulfate is a white solid.



Solid $\text{Fe}(\text{OH})_3$ forms when aqueous KOH and $\text{Fe}(\text{NO}_3)_3$ are mixed.

- b. Using the same procedures as in part a, we find that the ions present in the combined solution before any reaction occurs are Na^+ , SO_4^{2-} , Pb^{2+} , and NO_3^- . The possible salts that could form precipitates are



The compound NaNO_3 is soluble, but PbSO_4 is insoluble (see Rule 4 in Table 4.1). When these solutions are mixed, PbSO_4 will precipitate from the solution. The balanced equation is



- c. The combined solution (before any reaction occurs) contains the ions K^+ , OH^- , Fe^{3+} , and NO_3^- . The salts that might precipitate are KNO_3 and $\text{Fe}(\text{OH})_3$. The solubility rules in Table 4.1 indicate that both K^+ and NO_3^- salts are soluble. However, $\text{Fe}(\text{OH})_3$ is only slightly soluble (Rule 5) and hence will precipitate. The balanced equation is



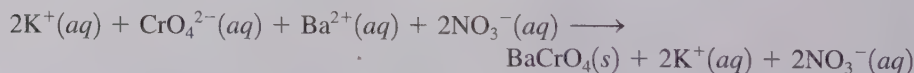
See Exercises 4.29 and 4.30.

4.6 Describing Reactions in Solution

In this section we will consider the types of equations used to represent reactions in solution. For example, when we mix aqueous potassium chromate with aqueous barium nitrate, a reaction occurs to form a precipitate (BaCrO_4) and dissolved potassium nitrate. So far we have written the **molecular equation** for this reaction:



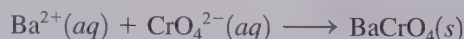
Although the molecular equation shows the reactants and products of the reaction, it does not give a very clear picture of what actually occurs in solution. As we have seen, aqueous solutions of potassium chromate, barium nitrate, and potassium nitrate contain individual ions, not molecules, as implied by the molecular equation. Thus the **complete ionic equation**



A strong electrolyte is a substance that completely breaks apart into ions when dissolved in water.

better represents the actual forms of the reactants and products in solution. *In a complete ionic equation, all substances that are strong electrolytes are represented as ions.*

The complete ionic equation reveals that only some of the ions participate in the reaction. The K^+ and NO_3^- ions are present in solution both before and after the reaction. The ions that do not participate directly in the reaction are called **spectator ions**. The ions that participate in this reaction are the Ba^{2+} and CrO_4^{2-} ions, which combine to form solid BaCrO_4 :



Net ionic equations include only those components that undergo changes in the reaction.

This equation, called the **net ionic equation**, includes only those solution components directly involved in the reaction. Chemists usually write the net ionic equation

tion for a reaction in solution because it gives the actual forms of the reactants and products and includes only the species that undergo a change.

Three Types of Equations Are Used to Describe Reactions in Solution

- The **molecular equation** gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants and products in solution.
- The **complete ionic equation** represents as ions all reactants and products that are strong electrolytes.
- The **net ionic equation** includes only those solution components undergoing a change. Spectator ions are not included.

SAMPLE EXERCISE 4.9

Writing Equations for Reactions

For each of the following reactions, write the molecular equation, the complete ionic equation, and the net ionic equation.

- Aqueous potassium chloride is added to aqueous silver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.
- Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

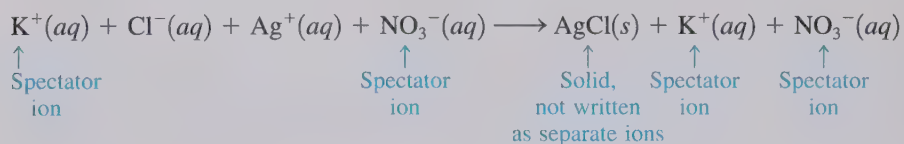
SOLUTION

a. Molecular Equation

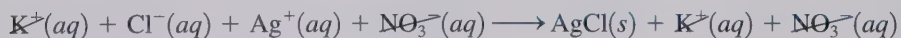


Complete Ionic Equation

(Remember: Any ionic compound dissolved in water will be present as the separated ions.)

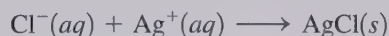


Canceling the spectator ions



gives the following net ionic equation.

Net Ionic Equation

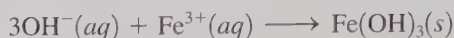


b. Molecular Equation



Complete Ionic Equation



Net Ionic Equation

See Exercises 4.31 through 4.36.

4.7 Stoichiometry of Precipitation Reactions

In Chapter 3 we covered the principles of chemical stoichiometry: the procedures for calculating quantities of reactants and products involved in a chemical reaction. Recall that in performing these calculations we first convert all quantities to moles and then use the coefficients of the balanced equation to assemble the appropriate mole ratios. In cases where reactants are mixed we must determine which reactant is limiting, since the reactant that is consumed first will limit the amounts of products formed. *These same principles apply to reactions that take place in solutions.* However, two points about solution reactions need special emphasis. The first is that it is sometimes difficult to tell immediately what reaction will occur when two solutions are mixed. Usually we must do some thinking about the various possibilities and then decide what probably will happen. The first step in this process *always* should be to write down the species that are actually present in the solution, as we did in Section 4.5. The second special point about solution reactions is that to obtain the moles of reactants we must use the volume of the solution and its molarity. This procedure was covered in Section 4.3.

We will introduce stoichiometric calculations for reactions in solution in Sample Exercise 4.10.

SAMPLE EXERCISE 4.10

Determining the Mass of Product Formed

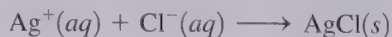
Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 M AgNO₃ solution to precipitate all the Ag⁺ ions in the form of AgCl.

SOLUTION

When added to the AgNO₃ solution (which contains Ag⁺ and NO₃[−] ions), the solid NaCl dissolves to yield Na⁺ and Cl[−] ions. Thus the mixed solution contains the ions



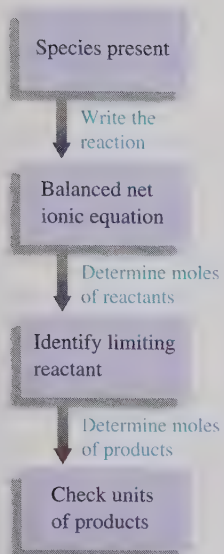
Note from Table 4.1 that NaNO₃ is soluble and AgCl is insoluble. Therefore, solid AgCl forms according to the following net ionic equation:



In this case we must add enough Cl[−] ions to react with all the Ag⁺ ions present. Thus we must calculate the moles of Ag⁺ ions present in 1.50 L of a 0.100 M AgNO₃ solution (remember that a 0.100 M AgNO₃ solution contains 0.100 M Ag⁺ ions and 0.100 M NO₃[−] ions):

$$1.50 \text{ L} \times \frac{0.100 \text{ mol Ag}^+}{\text{L}} = 0.150 \text{ mol Ag}^+$$

Because Ag⁺ and Cl[−] react in a 1:1 ratio, 0.150 mol Cl[−] ions and thus 0.150 mol NaCl are required. We calculate the mass of NaCl required as follows:



$$0.150 \text{ mol NaCl} \times \frac{58.45 \text{ g NaCl}}{\text{mol NaCl}} = 8.77 \text{ g NaCl}$$

See Exercise 4.39.

Notice from Sample Exercise 4.10 that the procedures for doing stoichiometric calculations for solution reactions are very similar to those for other types of reactions. It is useful to think in terms of the following steps for reactions in solution.

Solving Stoichiometry Problems for Reactions in Solution

- ➡ **1** Identify the species present in the combined solution, and determine what reaction occurs.
- ➡ **2** Write the balanced net ionic equation for the reaction.
- ➡ **3** Calculate the moles of reactants.
- ➡ **4** Determine which reactant is limiting.
- ➡ **5** Calculate the moles of product or products, as required.
- ➡ **6** Convert to grams or other units, as required.

SAMPLE EXERCISE 4.11

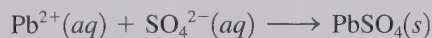
Determining the Mass of Product Formed

When aqueous solutions of Na_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, PbSO_4 precipitates. Calculate the mass of PbSO_4 formed when 1.25 L of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 2.00 L of 0.0250 M Na_2SO_4 are mixed.

SOLUTION

➡ **1** Identify the species present in the combined solution, and determine what reaction occurs. When the aqueous solutions of Na_2SO_4 (containing Na^+ and SO_4^{2-} ions) and $\text{Pb}(\text{NO}_3)_2$ (containing Pb^{2+} and NO_3^- ions) are mixed, the resulting solution contains the ions Na^+ , SO_4^{2-} , Pb^{2+} , and NO_3^- . Since NaNO_3 is soluble and PbSO_4 is insoluble (see Rule 4 in Table 4.1), solid PbSO_4 will form.

➡ **2** Write the balanced net ionic equation for the reaction. The net ionic equation is

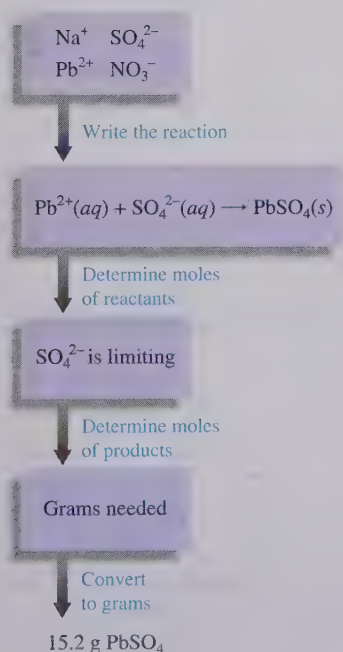


➡ **3** Calculate the moles of reactants. Since 0.0500 M $\text{Pb}(\text{NO}_3)_2$ contains 0.0500 M Pb^{2+} ions, we can calculate the moles of Pb^{2+} ions in 1.25 L of this solution as follows:

$$1.25 \text{ L} \times \frac{0.0500 \text{ mol Pb}^{2+}}{\text{L}} = 0.0625 \text{ mol Pb}^{2+}$$

The 0.0250 M Na_2SO_4 solution contains 0.0250 M SO_4^{2-} ions, and the number of moles of SO_4^{2-} ions in 2.00 L of this solution is

$$2.00 \text{ L} \times \frac{0.0250 \text{ mol SO}_4^{2-}}{\text{L}} = 0.0500 \text{ mol SO}_4^{2-}$$



➡ **4** *Determine which reactant is limiting.* Because Pb^{2+} and SO_4^{2-} react in a 1:1 ratio, the amount of SO_4^{2-} will be limiting (0.0500 mol SO_4^{2-} is less than 0.0625 mol Pb^{2+}).

➡ **5** *Calculate the moles of product.* Since the Pb^{2+} ions are present in excess, only 0.0500 mol of solid PbSO_4 will be formed.

➡ **6** *Convert to grams of product.* The mass of PbSO_4 formed can be calculated using the molar mass of PbSO_4 (303.3 g/mol):

$$0.0500 \text{ mol PbSO}_4 \times \frac{303.3 \text{ g PbSO}_4}{1 \text{ mol PbSO}_4} = 15.2 \text{ g PbSO}_4$$

See Exercises 4.41 and 4.42.

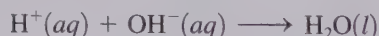
4.8 Acid–Base Reactions

Earlier in this chapter we considered Arrhenius's concept of acids and bases: An acid is a substance that produces H^+ ions when dissolved in water, and a base is a substance that produces OH^- ions. Although these ideas are fundamentally correct, it is convenient to have a more general definition of a base, which includes substances that do not contain OH^- ions. Such a definition was provided by Johannes N. Brønsted (1879–1947) and Thomas M. Lowry (1874–1936), who defined acids and bases as follows:

An **acid** is a proton donor.

A **base** is a proton acceptor.

How do we know when to expect an acid–base reaction? One of the most difficult tasks for someone inexperienced in chemistry is to predict what reaction might occur when two solutions are mixed. With precipitation reactions, we found that the best way to deal with this problem is to focus on the species actually present in the mixed solution. This idea also applies to acid–base reactions. For example, when an aqueous solution of hydrogen chloride (HCl) is mixed with an aqueous solution of sodium hydroxide (NaOH), the combined solution contains the ions H^+ , Cl^- , Na^+ , and OH^- . The separated ions are present because HCl is a strong acid and NaOH is a strong base. How can we predict what reaction occurs, if any? First, will NaCl precipitate? From Table 4.1 we can see that NaCl is soluble in water and thus will not precipitate. Therefore, the Na^+ and Cl^- ions are spectator ions. On the other hand, because water is a nonelectrolyte, large quantities of H^+ and OH^- ions cannot coexist in solution. They react to form H_2O molecules:



This is the net ionic equation for the reaction that occurs when aqueous solutions of HCl and NaOH are mixed.

Next, consider mixing an aqueous solution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) with an aqueous solution of potassium hydroxide (KOH). In our earlier discussion of conductivity we said that an aqueous solution of acetic acid is a weak electrolyte. This tells us that acetic acid does not dissociate into ions to any great extent. In fact, in 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ approximately 99% of the $\text{HC}_2\text{H}_3\text{O}_2$ molecules remain undissoci-



Understanding Concepts:
Acid–Base Reactions

The Brønsted–Lowry concept of acids and bases will be discussed in detail in Chapter 14.

ated. However, when solid KOH is dissolved in water, it dissociates completely to produce K^+ and OH^- ions. Therefore, in the solution formed by mixing aqueous solutions of $\text{HC}_2\text{H}_3\text{O}_2$ and KOH, *before any reaction occurs*, the principal species are $\text{HC}_2\text{H}_3\text{O}_2$, K^+ , and OH^- . What reaction will occur? A possible precipitation reaction could occur between K^+ and OH^- . However, we know that KOH is soluble, so precipitation does not occur. Another possibility is a reaction involving the hydroxide ion (a proton acceptor) and some proton donor. Is there a source of protons in the solution? The answer is yes—the $\text{HC}_2\text{H}_3\text{O}_2$ molecules. The OH^- ion has such a strong affinity for protons that it can strip them from the $\text{HC}_2\text{H}_3\text{O}_2$ molecules. The net ionic equation for this reaction is



This reaction illustrates a very important general principle: *The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid that we will encounter.* Of course, OH^- ions also react completely with the H^+ ions in solutions of strong acids.

We will now deal with the stoichiometry of acid–base reactions in aqueous solutions. The procedure is fundamentally the same as that used previously for precipitation reactions.

Performing Calculations for Acid–Base Reactions

- ➡ **1** List the species present in the combined solution *before any reaction occurs*, and decide what reaction will occur.
- ➡ **2** Write the balanced net ionic equation for this reaction.
- ➡ **3** Calculate the moles of reactants. For reactions in solution, use the volumes of the original solutions and their molarities.
- ➡ **4** Determine the limiting reactant where appropriate.
- ➡ **5** Calculate the moles of the required reactant or product.
- ➡ **6** Convert to grams or volume (of solution), as required.

An acid–base reaction is often called a **neutralization reaction**. When just enough base is added to react exactly with the acid in a solution, we say the acid has been *neutralized*.

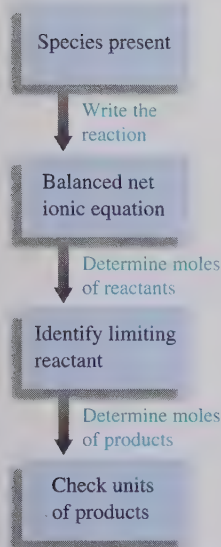
SAMPLE EXERCISE 4.12

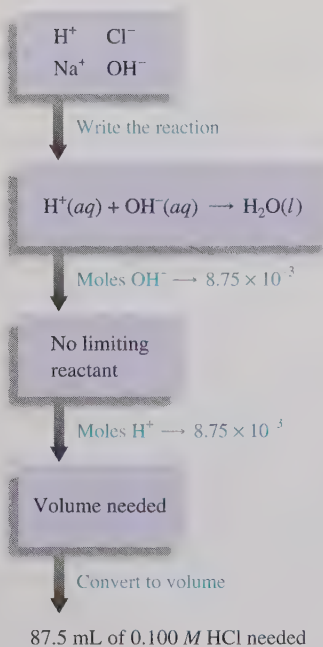
Neutralization Reactions I

What volume of a 0.100 M HCl solution is needed to neutralize 25.0 mL of 0.350 M NaOH?

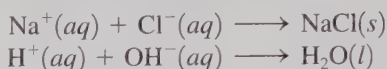
SOLUTION

- ➡ **1** List the species present in the combined solution *before any reaction occurs*, and decide what reaction will occur. The species present in the mixed solutions before any reaction occurs are



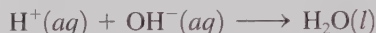


What reaction will occur? The two possibilities are



Since we know that NaCl is soluble, the first reaction does not take place (Na^+ and Cl^- are spectator ions). However, as we have seen before, the reaction of the H^+ and OH^- ions to form H_2O does occur.

➡ **2** Write the balanced net ionic equation. The balanced net ionic equation for this reaction is



➡ **3** Calculate the moles of reactants. The number of moles of OH^- ions in the 25.0-mL sample of 0.350 M NaOH is

$$25.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.350 \text{ mol OH}^-}{\text{L NaOH}} = 8.75 \times 10^{-3} \text{ mol OH}^-$$

➡ **4** Determine the limiting reactant. This problem requires the addition of just enough H^+ ions to react exactly with the OH^- ions present. Thus we need not be concerned with determining a limiting reactant.

➡ **5** Calculate the moles of reactant needed. Since H^+ and OH^- ions react in a 1:1 ratio, $8.75 \times 10^{-3} \text{ mol H}^+$ ions is required to neutralize the OH^- ions present.

➡ **6** Convert to volume required. The volume V of 0.100 M HCl required to furnish $8.75 \times 10^{-3} \text{ mol H}^+$ ions can be calculated as follows:

$$V \times \frac{0.100 \text{ mol H}^+}{\text{L}} = 8.75 \times 10^{-3} \text{ mol H}^+$$

Solving for V gives

$$V = \frac{8.75 \times 10^{-3} \text{ mol H}^+}{0.100 \text{ mol H}^+/\text{L}} = 8.75 \times 10^{-2} \text{ L}$$

Thus $8.75 \times 10^{-2} \text{ L}$ (87.5 mL) of 0.100 M HCl is required to neutralize 25.0 mL of 0.350 M NaOH.

See Exercises 4.49 and 4.50.

SAMPLE EXERCISE 4.13

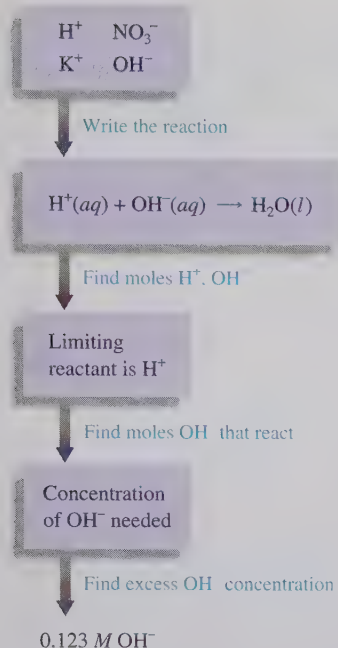
Neutralization Reactions II

In a certain experiment, 28.0 mL of 0.250 M HNO_3 and 53.0 mL of 0.320 M KOH are mixed. Calculate the amount of water formed in the resulting reaction. What is the concentration of H^+ or OH^- ions in excess after the reaction goes to completion?

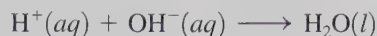
SOLUTION

The species available for reaction are





Since KNO_3 is soluble, K^+ and NO_3^- are spectator ions, so the net ionic equation is



We next compute the amounts of H^+ and OH^- ions present:

$$28.0 \text{ mL HNO}_3 \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol H}^+}{\text{L HNO}_3} = 7.00 \times 10^{-3} \text{ mol H}^+$$

$$53.0 \text{ mL KOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.320 \text{ mol OH}^-}{\text{L KOH}} = 1.70 \times 10^{-2} \text{ mol OH}^-$$

Since H^+ and OH^- react in a 1:1 ratio, the limiting reactant is H^+ . This means that $7.00 \times 10^{-3} \text{ mol H}^+$ ions will react with $7.00 \times 10^{-3} \text{ mol OH}^-$ ions to form $7.00 \times 10^{-3} \text{ mol H}_2\text{O}$.

The amount of OH^- ions in excess is obtained from the following difference:

$$\begin{aligned} \text{Original amount} - \text{amount consumed} &= \text{amount in excess} \\ 1.70 \times 10^{-2} \text{ mol OH}^- - 7.00 \times 10^{-3} \text{ mol OH}^- &= 1.00 \times 10^{-2} \text{ mol OH}^- \end{aligned}$$

The volume of the combined solution is the sum of the individual volumes:

$$\begin{aligned} \text{Original volume of HNO}_3 + \text{original volume of KOH} &= \text{total volume} \\ 28.0 \text{ mL} + 53.0 \text{ mL} &= 81.0 \text{ mL} = 8.10 \times 10^{-2} \text{ L} \end{aligned}$$

Thus the molarity of OH^- ions in excess is

$$\frac{\text{mol OH}^-}{\text{L solution}} = \frac{1.00 \times 10^{-2} \text{ mol OH}^-}{8.10 \times 10^{-2} \text{ L}} = 0.123 \text{ M OH}^-$$

See Exercises 4.51 and 4.52.

Acid-Base Titrations

Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration. A **titration** involves delivery (from a buret) of a measured volume of a solution of known concentration (the *titrant*) into a solution containing the substance being analyzed (the *analyte*). The titrant contains a substance that reacts in a known manner with the analyte. The point in the titration where enough titrant has been added to react exactly with the analyte is called the **equivalence point** or the **stoichiometric point**. This point is often marked by an **indicator**, a substance added at the beginning of the titration that changes color at (or very near) the equivalence point. The point where the indicator *actually* changes color is called the **endpoint** of the titration. The goal is to choose an indicator such that the endpoint (where the indicator changes color) occurs exactly at the equivalence point (where just enough titrant has been added to react with all the analyte).

The following three requirements must be met for a titration to be successful:

1. The exact reaction between titrant and analyte must be known (and rapid).
2. The stoichiometric (equivalence) point must be marked accurately.
3. The volume of titrant required to reach the stoichiometric point must be known accurately.

When the analyte is a base or an acid, the required titrant is a strong acid or strong base, respectively. This procedure is called an *acid-base titration*. An

Ideally, the endpoint and stoichiometric point should coincide.

**FIGURE 4.18**

The titration of an acid with a base.

(a) The titrant (the base) is in the buret, and the beaker contains the acid solution along with a small amount of indicator. (b) As base is added drop by drop to the acid solution in the beaker during the titration, the indicator changes color, but the color disappears on mixing. (c) The stoichiometric (equivalence) point is marked by a permanent indicator color change. The volume of base added is the difference between the final and initial buret readings.

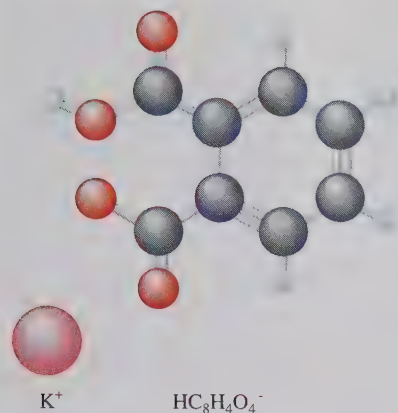
indicator very commonly used for acid–base titrations is phenolphthalein, which is colorless in an acidic solution and pink in a basic solution. Thus, when an acid is titrated with a base, the phenolphthalein remains colorless until after the acid is consumed and the first drop of excess base is added. In this case, the endpoint (the solution changes from colorless to pink) occurs approximately one drop of base beyond the stoichiometric point. This type of titration is illustrated in the three photos in Fig. 4.18.

We will deal with the acid–base titrations only briefly here but will return to the topic of titrations and indicators in more detail in Chapter 15. The titration of an acid with a standard solution containing hydroxide ions is described in Sample Exercise 4.15. In Sample Exercise 4.14 we show how to determine accurately the concentration of a sodium hydroxide solution. This procedure is called *standardizing the solution*.

SAMPLE EXERCISE 4.14

Neutralization Titration

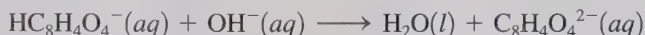
A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution. To do this, the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, often abbreviated KHP). KHP (molar mass 204.22 g/mol) has one acidic hydrogen. The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint. The dif-



ference between the final and initial buret readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP. Calculate the concentration of the sodium hydroxide solution.

SOLUTION

Aqueous sodium hydroxide contains the Na^+ and OH^- ions, and $KHC_8H_4O_4$ dissolves in water to give the K^+ and $HC_8H_4O_4^-$ ions. As the titration proceeds, the mixed solution contains the following ions: K^+ , $HC_8H_4O_4^-$, Na^+ , and OH^- . The OH^- will remove an H^+ from the $HC_8H_4O_4^-$ to give the following net ionic reaction:



Since the reaction exhibits 1:1 stoichiometry, we know that 41.20 mL of the sodium hydroxide solution must contain exactly the same number of moles of OH^- as there are moles of $HC_8H_4O_4^-$ in 1.3009 g $KHC_8H_4O_4$.

We calculate the moles of $KHC_8H_4O_4$ in the usual way:

$$1.3009 \text{ g } KHC_8H_4O_4 \times \frac{1 \text{ mol } KHC_8H_4O_4}{204.22 \text{ g } KHC_8H_4O_4} = 6.3701 \times 10^{-3} \text{ mol } KHC_8H_4O_4$$

This means that 6.3701×10^{-3} mol OH^- must be added to react with the 6.3701×10^{-3} mol $HC_8H_4O_4^-$. Thus 41.20 mL (4.120×10^{-2} L) of the sodium hydroxide solution must contain 6.3701×10^{-3} mol OH^- (and Na^+), and the concentration of the sodium hydroxide solution is

$$\begin{aligned} \text{Molarity of NaOH} &= \frac{\text{mol NaOH}}{\text{L solution}} = \frac{6.3701 \times 10^{-3} \text{ mol NaOH}}{4.120 \times 10^{-2} \text{ L}} \\ &= 0.1546 \text{ M} \end{aligned}$$

This standard sodium hydroxide solution can now be used in other experiments (see Sample Exercise 4.15).

See Exercises 4.53, 4.54, and 4.56.

SAMPLE EXERCISE 4.15

Neutralization Analysis

An environmental chemist analyzed the effluent (the released waste material) from an industrial process known to produce the compounds carbon tetrachloride (CCl_4) and benzoic acid ($HC_7H_5O_2$), a weak acid that has one acidic hydrogen atom per molecule. A sample of this effluent weighing 0.3518 g was shaken with water, and the resulting aqueous solution required 10.59 mL of 0.1546 M NaOH for neutralization. Calculate the mass percent of $HC_7H_5O_2$ in the original sample.

SOLUTION

In this case, the sample was a mixture containing CCl_4 and $HC_7H_5O_2$, and it was titrated with OH^- ions. Clearly, CCl_4 is not an acid (it contains no hydrogen atoms), so we can assume it does not react with OH^- ions. However, $HC_7H_5O_2$ is an acid that donates one H^+ ion per molecule to react with an OH^- ion as follows:



Although $HC_7H_5O_2$ is a weak acid, the OH^- ion is such a strong base that we can assume that each OH^- ion added will react with a $HC_7H_5O_2$ molecule until all the benzoic acid is consumed.

We must first determine the number of moles of OH^- ions required to react with all the $\text{HC}_7\text{H}_5\text{O}_2$:

$$10.59 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1546 \text{ mol OH}^-}{\text{L NaOH}} = 1.637 \times 10^{-3} \text{ mol OH}^-$$

This number is also the number of moles of $\text{HC}_7\text{H}_5\text{O}_2$ present. The number of grams of the acid is calculated using its molar mass (122.12 g/mol):

$$1.637 \times 10^{-3} \text{ mol HC}_7\text{H}_5\text{O}_2 \times \frac{122.12 \text{ g HC}_7\text{H}_5\text{O}_2}{1 \text{ mol HC}_7\text{H}_5\text{O}_2} = 0.1999 \text{ g HC}_7\text{H}_5\text{O}_2$$

The mass percent of $\text{HC}_7\text{H}_5\text{O}_2$ in the original sample is

$$\frac{0.1999 \text{ g}}{0.3518 \text{ g}} \times 100 = 56.82\%$$

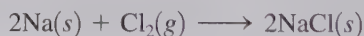
See Exercise 4.55.

The first step in the analysis of a complex solution is to write down the components and focus on the chemistry of each one.

In doing problems involving titrations, you must first decide what reaction is occurring. Sometimes this seems difficult because the titration solution contains several components. *The key to success is to first write down all the components in the solution and focus on the chemistry of each one.* We have been emphasizing this approach in dealing with the reactions between ions in solution. Make it a habit to write down the components of solutions before trying to decide what reaction(s) might take place as you attempt the end-of-chapter problems involving titrations.

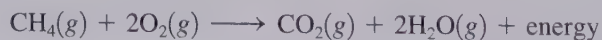
4.9 Oxidation–Reduction Reactions

We have seen that many important substances are ionic. Sodium chloride, for example, can be formed by the reaction of elemental sodium and chlorine:



In this reaction, solid sodium, which contains neutral sodium atoms, reacts with chlorine gas, which contains diatomic Cl_2 molecules, to form the ionic solid NaCl , which contains Na^+ and Cl^- ions. This process is represented in Fig. 4.19. *Reactions like this one, in which one or more electrons are transferred, are called oxidation–reduction reactions or redox reactions.*

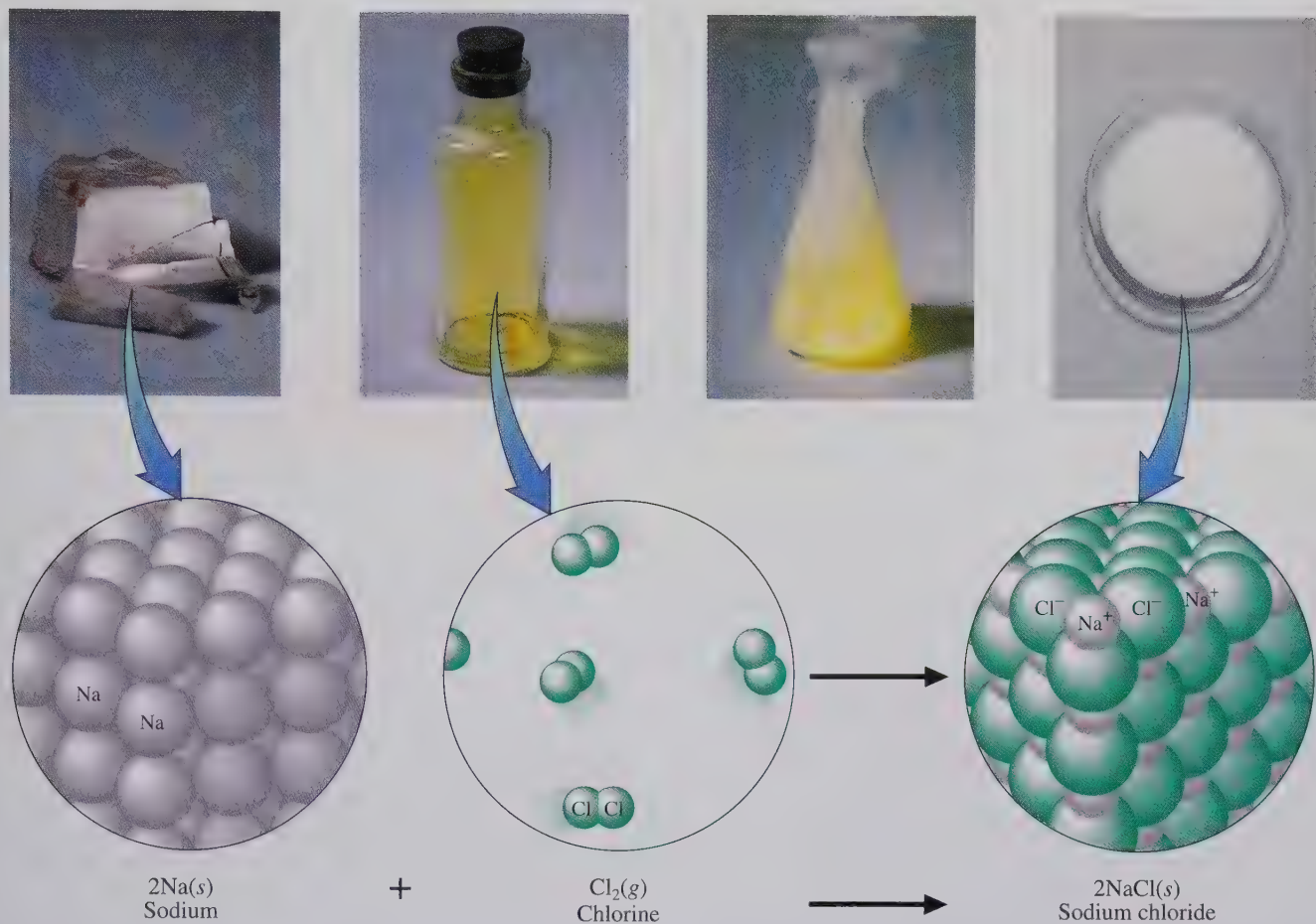
Many important chemical reactions involve oxidation and reduction. Photosynthesis, which stores energy from the sun in plants by converting carbon dioxide and water to sugar, is a very important oxidation–reduction reaction. In fact, most reactions used for energy production are redox reactions. In humans, the oxidation of sugars, fats, and proteins provides the energy necessary for life. Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction. An example is the reaction of methane with oxygen:



Even though none of the reactants or products in this reaction is ionic, the reaction is still assumed to involve a transfer of electrons from carbon to oxygen. To explain this, we must introduce the concept of oxidation states.



Understanding Concepts:
Oxidation–Reduction Reactions

**FIGURE 4.19**

The reaction of solid sodium and gaseous chlorine to form solid sodium chloride.

Oxidation States

The concept of **oxidation states** (also called *oxidation numbers*) provides a way to keep track of electrons in oxidation–reduction reactions, particularly redox reactions involving covalent substances. Recall that electrons are shared by atoms in covalent bonds. The oxidation states of atoms in covalent compounds are obtained by arbitrarily assigning the electrons (which are actually shared) to particular atoms. We do this as follows: For a covalent bond between two identical atoms, the electrons are split equally between the two. In cases where two different atoms are involved (and the electrons are thus shared unequally), the shared electrons are assigned completely to the atom that has the stronger attraction for electrons. For example, recall from the discussion of the water molecule in Section 4.1 that oxygen has a greater attraction for electrons than does hydrogen. Therefore, in assigning the oxidation state of oxygen and hydrogen in H_2O , we assume that the oxygen atom actually possesses all the electrons. Recall that a hydrogen atom has one electron. Thus, in water, oxygen has formally “taken” the electrons from two hydrogen atoms. This gives the oxygen an *excess* of two electrons (its oxidation state is -2) and

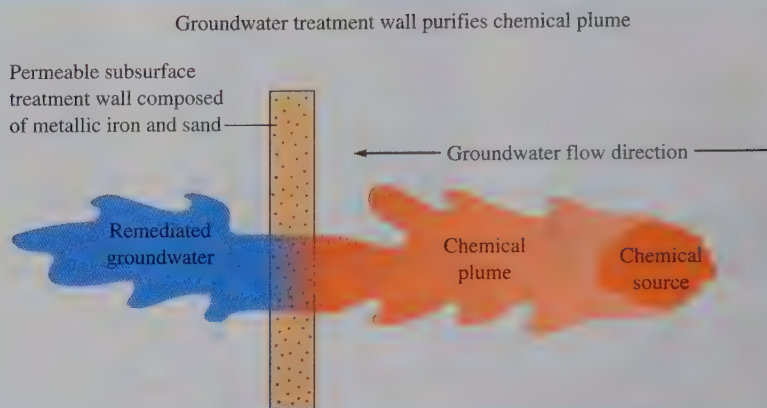
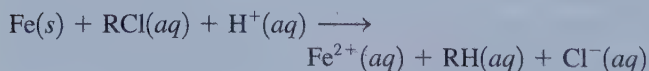
CHEMICAL IMPACT

Iron Zeroes in on Pollution

Treating groundwater contaminated with pollutants is typically very complicated and very expensive. However, chemists have discovered a low-tech, economical method for treating the contaminated groundwater near a former semiconductor manufacturing plant in Sunnyvale, California. They have replaced the elaborate decontamination machinery used at the site for more than a decade with 220 tons of iron filings buried in a giant trough. Because there are no pumps to maintain and no electricity to purchase, this simple system will save approximately \$300,000 per year. The property, which was thought to be unusable for the 30-year lifetime of the old clean-up process because of the need for constant monitoring and access, can now be used immediately.

A schematic of the iron treatment method is shown in the accompanying figure. At Sunnyvale, the iron barrier is 40 feet long, 4 feet wide, and 20 feet deep. In the 4 days it takes for contaminated water to seep through the wall of iron, the chlorinated organic contaminants are degraded into products that are then themselves decomposed to simpler substances. According to engineers on the site, the polluted water that seeps through the wall meets Environmental Protection Agency (EPA) standards when it emerges on the other side.

How does iron metal clean up contaminated groundwater? It's a result of the ability of iron metal (oxidation state = 0) to act as a reducing agent toward the chlorine-containing organic pollutant molecules. The reaction can be represented as follows:



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where RCl represents a chlorinated organic molecule. The reaction appears to involve a direct reaction between the metal and an RCl molecule adsorbed on the metal surface.

In addition to decomposing chlorinated organic contaminants, iron appears to be useful against other pollutants as well. Iron can degrade dye wastes from textile mills and can reduce soluble Cr(VI) compounds to insoluble Cr(III) products, which are much less harmful. Iron's reducing abilities also appear useful in removing radioactive technetium, a common pollutant at nuclear processing facilities. Iron also appears to be effective for removing nitrates from the soil.

Other metals, such as zinc, tin, and palladium, also have shown promise for use in groundwater clean-up. These metals generally react more quickly than iron but are more expensive and pose their own environmental hazards.

Inexpensive and environmentally benign, iron seems to be the metal of choice for most groundwater clean-up. It's cheap, it's effective, it's almost a miracle!

leaves each hydrogen with no electrons (the oxidation state of each hydrogen is thus +1).

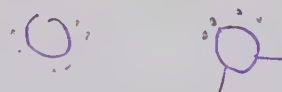
We define the *oxidation states* (or *oxidation numbers*) of the atoms in a covalent compound as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons. Of course, for ionic compounds containing monatomic ions, the oxidation states of the ions are equal to the ion charges.

TABLE 4.2 Rules for Assigning Oxidation States

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	$\text{Na}(s)$, $\text{O}_2(g)$, $\text{O}_3(g)$, $\text{Hg}(l)$
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+ , Cl^-
• Fluorine is -1 in its compounds	Fluorine: -1	HF , PF_3
• Oxygen is usually -2 in its compounds Exception: peroxides (containing O_2^{2-}) in which oxygen is -1	Oxygen: -2	H_2O , CO_2
• Hydrogen is $+1$ in its covalent compounds	Hydrogen: $+1$	H_2O , HCl , NH_3



Oxidation of copper metal by nitric acid. The copper atoms lose two electrons to form Cu^{2+} ions, which give a deep green color that becomes turquoise when diluted with water.



These considerations lead to a series of rules for assigning oxidation states that are summarized in Table 4.2. Application of these simple rules allows the assignment of oxidation states in most compounds. To apply these rules recognize that the sum of the oxidation states must be zero for an electrically neutral compound. For an ion, the sum of the oxidation states must equal the charge of the ion. The principles are illustrated by Sample Exercise 4.16.

It is worthwhile to note at this point that the convention is to write actual charges on ions as $n+$ or $n-$, the number being written *before* the plus or minus sign. On the other hand, oxidation states (not actual charges) are written $+n$ or $-n$, the number being written *after* the plus or minus sign.

SAMPLE EXERCISE 4.16

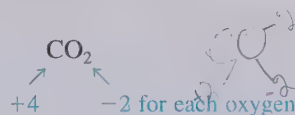
Assigning Oxidation States

Assign oxidation states to all atoms in the following.

- CO_2
- SF_6
- NO_3^-

SOLUTION

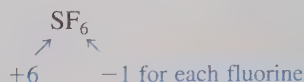
- Since we have a specific rule for the oxidation state of oxygen, we will assign its value first. The oxidation state of oxygen is -2 . The oxidation state of the carbon atom can be determined by recognizing that since CO_2 has no charge, the sum of the oxidation states for oxygen and carbon must be zero. Since each oxygen is -2 and there are two oxygen atoms, the carbon atom must be assigned an oxidation state of $+4$:



We can check the assigned oxidation states by noting that when the number of atoms is taken into account, the sum is zero as required:

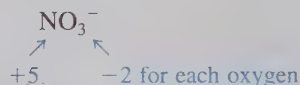
$$\begin{array}{ccc} & 1(+4) & + 2(-2) = 0 \\ \nearrow & & \uparrow \\ \text{No. of C} & & \text{No. of O} \\ \text{atoms} & & \text{atoms} \end{array}$$

- b. Since we have no rule for sulfur, we first assign the oxidation state of each fluorine as -1 . The sulfur must then be assigned an oxidation state of $+6$ to balance the total of -6 from the fluorine atoms:



CHECK: $+6 + 6(-1) = 0$

- c. Oxygen has an oxidation state of -2 . Because the sum of the oxidation states of the three oxygens is -6 and the net charge on the NO_3^- ion is $1-$, the nitrogen must have an oxidation state of $+5$:



CHECK: $+5 + 3(-2) = -1$

Note that in this case the sum must be -1 (the overall charge on the ion).

See Exercises 4.57 through 4.60.

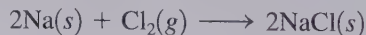


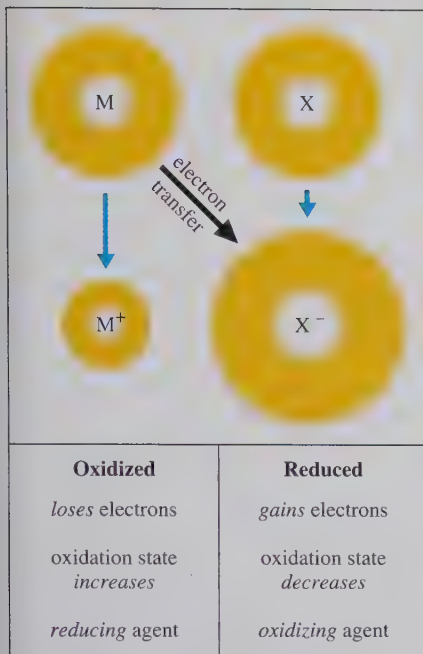
Magnetite is a magnetic ore containing Fe_3O_4 . Note that the compass needle points toward the ore.

We need to make one more point about oxidation states, and this can be illustrated by the compound Fe_3O_4 , which is the main component in magnetite, an iron ore that accounts for the reddish color of many types of rocks and soils. To determine the oxidation states in Fe_3O_4 , we first assign each oxygen atom its usual oxidation state of -2 . The three iron atoms must yield a total of $+8$ to balance the total of -8 from the four oxygens. This means that each iron atom has an oxidation state of $+\frac{8}{3}$. A noninteger value for the oxidation state may seem strange because charge is expressed in whole numbers. However, although they are rare, noninteger oxidation states do occur because of the rather arbitrary way that electrons are divided up by the rules in Table 4.2. For Fe_3O_4 , for example, the rules assume that all the iron atoms are equal, when in fact this compound can best be viewed as containing four O^{2-} ions, two Fe^{3+} ions, and one Fe^{2+} ion per formula unit. (Note that the “average” charge on iron works out to be $\frac{8}{3}+$, which is equal to the oxidation state we determined above.) Noninteger oxidation states should not intimidate you. They are used in the same way as integer oxidation states—for keeping track of electrons.

The Characteristics of Oxidation–Reduction Reactions

Oxidation–reduction reactions are characterized by a transfer of electrons. In some cases, the transfer occurs in a literal sense to form ions, such as in the reaction



**FIGURE 4.20**

A summary of an oxidation–reduction process, in which M is oxidized and X is reduced.

Oxidation is an increase in oxidation state.
Reduction is a decrease in oxidation state.

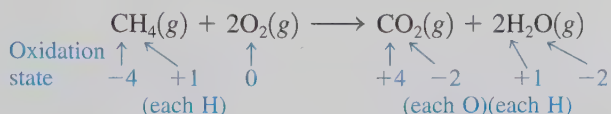
A helpful mnemonic device is **OIL RIG** (**O**xidation **I**nvolves **L**oss; **R**eduction **I**nvolves **G**ain). Another common mnemonic is **LEO says GER**. (**L**oss of **E**lectrons, **O**xidation; **G**ain of **E**lectrons, **R**eduction).

An oxidizing agent is reduced and a reducing agent is oxidized in a redox reaction.

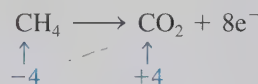


Visualization: Zinc and Iodine

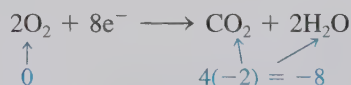
However, sometimes the transfer is less obvious. For example, consider the combustion of methane (the oxidation state for each atom is given):



Note that the oxidation state for oxygen in O_2 is 0 because it is in elemental form. In this reaction there are no ionic compounds, but we can still describe the process in terms of a transfer of electrons. Note that carbon undergoes a change in oxidation state from -4 in CH_4 to $+4$ in CO_2 . Such a change can be accounted for by a loss of eight electrons (the symbol e^- stands for an electron);

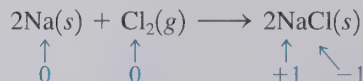


On the other hand, each oxygen changes from an oxidation state of 0 in O_2 to -2 in H_2O and CO_2 , signifying a gain of two electrons per atom. Since four oxygen atoms are involved, this is a gain of eight electrons:



No change occurs in the oxidation state of hydrogen, and it is not formally involved in the electron-transfer process.

With this background, we can now define some important terms. **Oxidation** is an *increase* in oxidation state (a loss of electrons). **Reduction** is a *decrease* in oxidation state (a gain of electrons). Thus in the reaction



sodium is oxidized and chlorine is reduced. In addition, Cl_2 is called the **oxidizing agent (electron acceptor)**, and Na is called the **reducing agent (electron donor)**. These terms are summarized in Fig. 4.20.

Concerning the reaction



we can say the following:

Carbon is oxidized because there has been an increase in its oxidation state (carbon has formally lost electrons).

Oxygen is reduced because there has been a decrease in its oxidation state (oxygen has formally gained electrons).

CH_4 is the reducing agent.

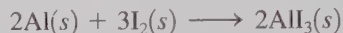
O_2 is the oxidizing agent.

Note that when the oxidizing or reducing agent is named, the *whole compound* is specified, not just the element that undergoes the change in oxidation state.

SAMPLE EXERCISE 4.17

Oxidation–Reduction Reactions I

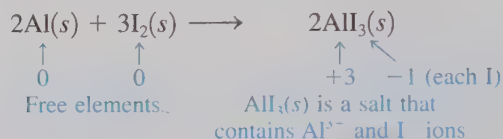
When powdered aluminum metal is mixed with pulverized iodine crystals and a drop of water is added to help the reaction get started, the resulting reaction produces a great deal of energy. The mixture bursts into flames, and a purple smoke of I_2 vapor is produced from the excess iodine. The equation for the reaction is



For this reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

SOLUTION

The first step is to assign oxidation states:



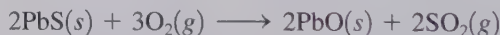
Since each aluminum atom changes its oxidation state from 0 to +3 (an increase in oxidation state), aluminum is *oxidized*. On the other hand, the oxidation state of each iodine atom decreases from 0 to −1, and iodine is *reduced*. Since Al furnishes electrons for the reduction of iodine, it is the *reducing agent*; I_2 is the *oxidizing agent*.

See Exercises 4.61 and 4.62.

SAMPLE EXERCISE 4.18

Oxidation–Reduction Reactions II

Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions. In the metallurgy of galena (PbS), the principal lead-containing ore, the first step is the conversion of lead sulfide to its oxide (a process called *roasting*):



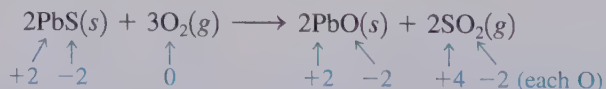
The oxide is then treated with carbon monoxide to produce the free metal:



For each reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

SOLUTION

For the first reaction, we can assign the following oxidation states:



The oxidation state for the sulfur atom increases from −2 to +4. Thus sulfur is oxidized. The oxidation state for each oxygen atom decreases from 0 to −2. Oxygen is reduced. The oxidizing agent (that accepts the electrons) is O_2 , and the reducing agent (that donates electrons) is PbS .



Finely ground aluminum and iodine are mixed and react vigorously to form aluminum iodide after a drop of water is added. The purple cloud is excess iodine vaporized by the heat of the reaction.

CHEMICAL IMPACT

Aging: Does It Involve Oxidation?

Although aging is supposed to bring wisdom, almost no one wants to get old. Along with wisdom, aging brings wrinkles, loss of physical strength, and greater susceptibility to disease.

Why do we age? No one knows for certain, but many scientists think that oxidation plays a major role. The oxygen molecule and other oxidizing agents in the body apparently can extract single electrons from the large molecules that make up cell membranes, thus making them very reactive. Subsequently, these activated molecules can link up, changing the properties of the cell membrane. At some point, enough of these reactions have occurred that the body's immune system comes to view the changed cell as an "enemy" and destroys it. This is particularly detrimental to the organism when the cells involved are irreplaceable. Nerve cells, for example, fall into this category. They rarely regenerate in an adult.

The body has defenses against oxidation, such as vitamin E, a well-known antioxidant. Studies have shown that red blood cells age much faster than normal when they are deficient in vitamin E. Based on studies such as these, some have suggested large doses of vitamin E as a preventive measure against aging, but there is no solid evidence that this practice has any impact on aging.

Another protective antioxidant found in our bodies is superoxide dismutase [SOD], which protects us from the superoxide ion O_2^- , a powerful oxidizing agent that is particularly damaging to vital enzymes. The importance of SOD in opposing the aging process is indicated from the results of a study by Dr. Richard Cutler at the Gerontology Research Center of the National Institutes of Health in Baltimore that showed a strong correlation between the life spans of a dozen mammalian species and their levels of SOD. Human SOD is now being produced by the techniques of biotechnology

in amounts that will enable scientists to carefully study its effects on aging and on various diseases such as rheumatoid arthritis and muscular dystrophy. Although SOD is available in health food stores in forms to be taken orally, this practice is useless because the SOD is digested (broken down into simpler substances) before it can reach the bloodstream.

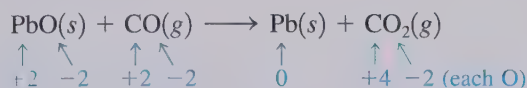
Research does indicate that consuming certain foods may retard the aging process. For example, a recent study of 8000 male Harvard graduates found that chocolate and candy eaters live almost a year longer than those who abstain. Although the researchers from Harvard School of Public Health are not certain of the mechanism for this effect, they suggest that the antioxidants present in chocolate may provide the health benefits. For example, chocolate contains phenols, antioxidants that are also present in wine, another substance that seems to promote good health if used in moderation.

Oxidation is only one possible cause for aging. Research continues on many fronts to try to discover why we get "older" as time passes.



Can eating chocolate slow down the aging process?

For the second reaction we have



Lead is reduced (its oxidation state decreases from +2 to 0), and carbon is oxidized (its oxidation state increases from +2 to +4). PbO is the oxidizing agent, and CO is the reducing agent.

See Exercises 4.61 and 4.62.

4.10 Balancing Oxidation–Reduction Equations

Oxidation–reduction reactions in aqueous solutions are often complicated, which means that it can be difficult to balance their equations by simple inspection. In this section we will discuss a special technique for balancing the equations of redox reactions that occur in aqueous solutions. It is called the *half-reaction method*.

The Half-Reaction Method for Balancing Oxidation–Reduction Reactions in Aqueous Solutions

For oxidation–reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions**: one involving oxidation and the other involving reduction. For example, consider the unbalanced equation for the oxidation–reduction reaction between cerium(IV) ion and tin(II) ion:



This reaction can be separated into a half-reaction involving the substance being *reduced*,



and one involving the substance being *oxidized*,

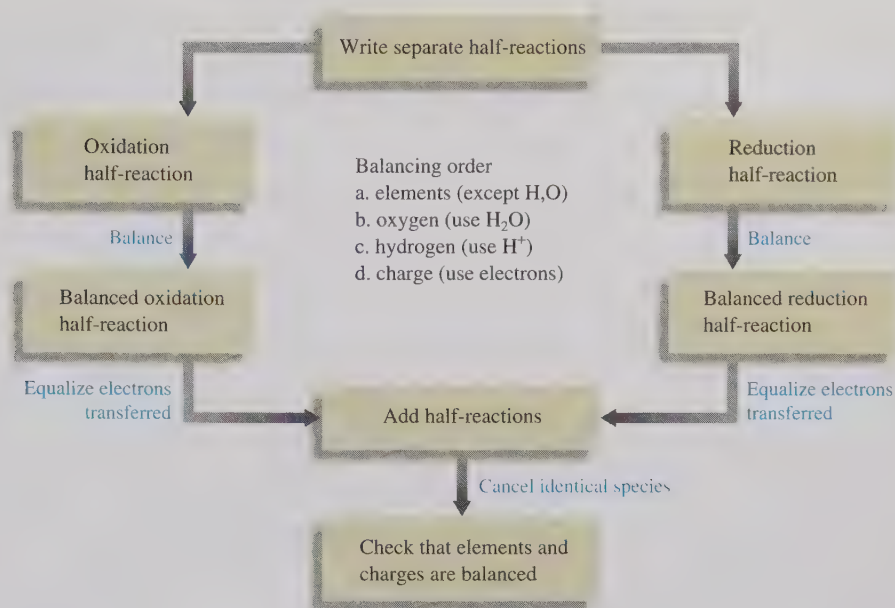


The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation. The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Acidic Solution

- ➡ **1** Write separate equations for the oxidation and reduction half-reactions.
- ➡ **2** For each half-reaction,
 - a. Balance all the elements except hydrogen and oxygen.
 - b. Balance oxygen using H_2O .
 - c. Balance hydrogen using H^+ .
 - d. Balance the charge using electrons.
- ➡ **3** If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.
- ➡ **4** Add the half-reactions, and cancel identical species.
- ➡ **5** Check that the elements and charges are balanced.

These steps are summarized by the following flow chart:

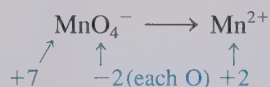


We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

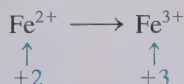


This reaction can be used to analyze iron ore for its iron content.

➡ **1** *Identify and write equations for the half-reactions.* The oxidation states for the half-reaction involving the permanganate ion show that manganese is reduced:



This is the *reduction half-reaction*. The other half-reaction involves the oxidation of iron(II) to iron(III) ion and is the *oxidation half-reaction*:



➡ **2** *Balance each half-reaction.* For the reduction reaction, we have



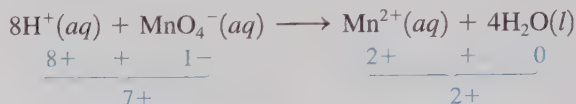
- The manganese is balanced.
- We balance oxygen by adding 4H₂O to the right side of the equation:



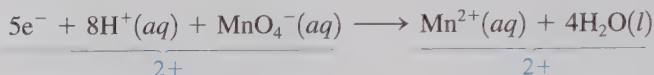
- Next, we balance hydrogen by adding 8H⁺ to the left side:



- d. All the elements have been balanced, but we need to balance the charge using electrons. At this point we have the following overall charges for reactants and products in the reduction half-reaction:



We can equalize the charges by adding five electrons to the left side:

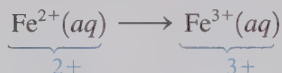


Both the *elements* and the *charges* are now balanced, so this represents the balanced reduction half-reaction. The fact that five electrons appear on the reactant side of the equation makes sense, since five electrons are required to reduce MnO_4^- (Mn has an oxidation state of +7) to Mn^{2+} (Mn has an oxidation state of +2).

For the oxidation reaction



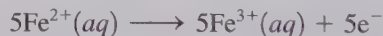
the elements are balanced, and we must simply balance the charge:



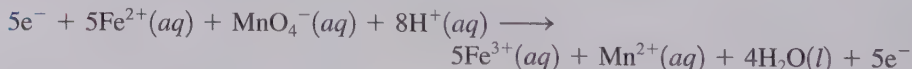
One electron is needed on the right side to give a net 2+ charge on both sides:



➡ **3** *Equalize the electron transfer in the two half-reactions.* Since the reduction half-reaction involves a transfer of five electrons and the oxidation half-reaction involves a transfer of only one electron, the oxidation half-reaction must be multiplied by 5:



➡ **4** *Add the half-reactions.* The half-reactions are added to give



Note that the electrons cancel (as they must) to give the final balanced equation:



➡ **5** *Check that elements and charges are balanced.*

Elements balance: $5\text{Fe}, 1\text{Mn}, 4\text{O}, 8\text{H} \longrightarrow 5\text{Fe}, 1\text{Mn}, 4\text{O}, 8\text{H}$

Charges balance: $5(2+) + (1-) + 8(1+) = 17+ \longrightarrow 5(3+) + (2+) + 0 = 17+$

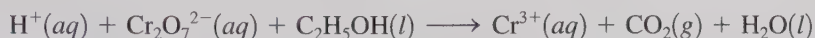
The equation is balanced.

The number of electrons gained in the reduction half-reaction must equal the number of electrons lost in the oxidation half-reaction.

SAMPLE EXERCISE 4.19

Balancing Oxidation–Reduction Reactions (Acidic)

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) as follows:



Balance this equation using the half-reaction method.

SOLUTION

➡ **1** The reduction half-reaction is



Chromium is reduced from an oxidation state of +6 in $\text{Cr}_2\text{O}_7^{2-}$ to one of +3 in Cr^{3+} .

The oxidation half-reaction is



Carbon is oxidized from an oxidation state of -2 in $\text{C}_2\text{H}_5\text{OH}$ to $+4$ in CO_2 .

➡ **2** Balancing all elements except hydrogen and oxygen in the first half-reaction, we have



(left) Acidified potassium dichromate is added to a beaker of ethyl alcohol.
(right) Potassium dichromate is reduced to a blue-violet solution of Cr^{3+} ions by ethyl alcohol.

Balancing oxygen using H_2O , we have



Balancing hydrogen using H^+ , we have



Balancing the charge using electrons, we have



Next, we turn to the oxidation half-reaction



Balancing carbon, we have



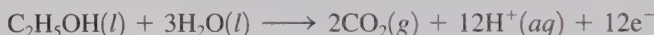
Balancing oxygen using H_2O , we have



Balancing hydrogen using H^+ , we have



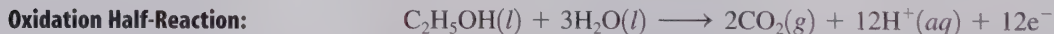
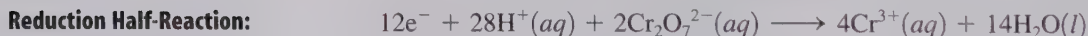
We then balance the charge by adding 12e^- to the right side:



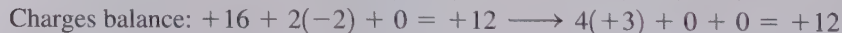
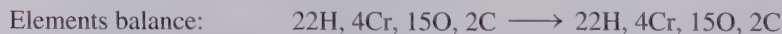
➡ **3** In the reduction half-reaction there are 6 electrons on the left-hand side, and there are 12 electrons on the right-hand side of the oxidation half-reaction. Thus we multiply the reduction half-reaction by 2 to give



➡ **4** Adding the half-reactions and canceling identical species, we have



➡ **5** Check that elements and charges are balanced.



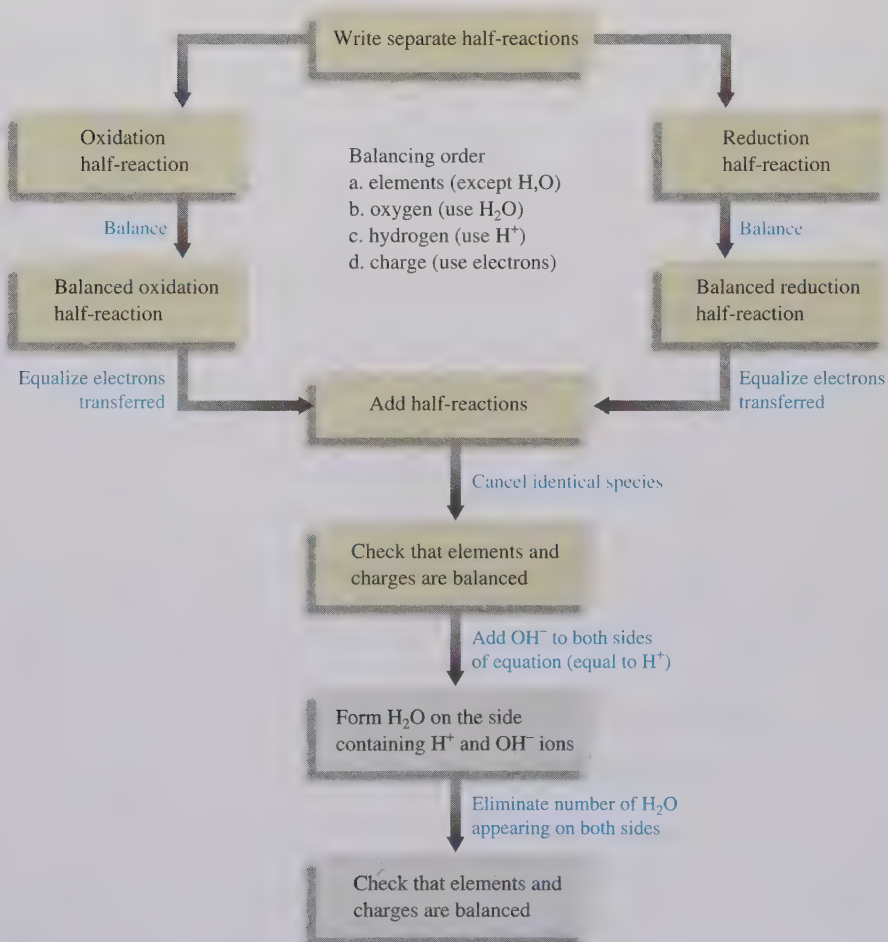
See Exercises 4.63 and 4.64.

Oxidation–reduction reactions can occur in basic solutions (the reactions involve OH^- ions) as well as in acidic solution (the reactions involve H^+ ions). The half-reaction method for balancing equations is slightly different for the two cases.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Basic Solution

- ➔ **1** Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present*.
- ➔ **2** To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O .)
- ➔ **3** Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.
- ➔ **4** Check that elements and charges are balanced.

This method is summarized by the following flow chart:

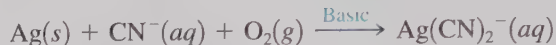


We will illustrate how this method is applied in Sample Exercise 4.20.

SAMPLE EXERCISE 4.20

Balancing Oxidation–Reduction Reactions (Basic)

Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction that occurs in basic solution:



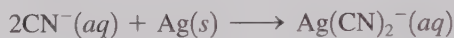
Balance this equation using the half-reaction method.

SOLUTION

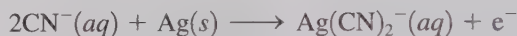
➡ **1** Balance the equation as if H^+ ions were present. Balance the oxidation half-reaction:



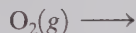
Balance carbon and nitrogen:



Balance the charge:



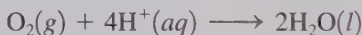
Balance the reduction half-reaction:



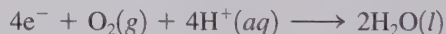
Balance oxygen:



Balance hydrogen:



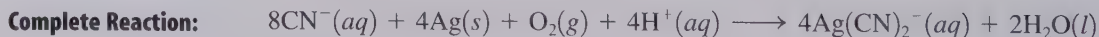
Balance the charge:



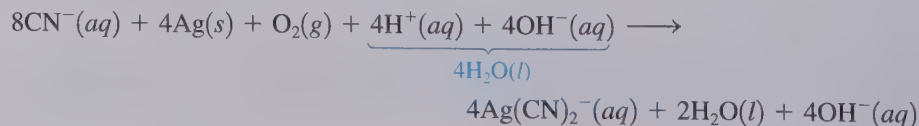
Multiply the balanced oxidation half-reaction by 4:



Add the half-reactions, and cancel identical species:



➡ **2** Add OH^- ions to both sides of the balanced equation to eliminate the H^+ ions. We need to add 4OH^- to each side:



➡ **3** Eliminate as many H_2O molecules as possible:



➡ **4** Check that elements and charges are balanced.

Elements balance: $8\text{C}, 8\text{N}, 4\text{Ag}, 4\text{O}, 4\text{H} \longrightarrow 8\text{C}, 8\text{N}, 4\text{Ag}, 4\text{O}, 4\text{H}$

Charges balance: $8(1-) + 0 + 0 + 0 = 8- \longrightarrow 4(1-) + 4(1-) = 8-$

See Exercises 4.65 and 4.66.

For Review

Summary

Many important chemical reactions occur in aqueous solutions. Water is a good solvent for ionic solids because the polar water molecules interact with the ions. This assists in the dissolving process. One characteristic property of a solution is its electrical conductivity. Solutions of strong electrolytes conduct current easily because there is 100% dissociation to ions. Weak electrolytes dissociate only to a small extent and their solutions exhibit low conductivity. Nonelectrolytes produce no ions when they dissolve and conduct no current.

The Arrhenius definition regards an acid as a substance that produces H^+ ions (protons) in solution; a base is a substance that produces OH^- ions. The Brønsted–Lowry concept defines an acid as a proton donor and a base as a proton acceptor. A strong acid dissociates completely in water, and a weak acid dissociates only very slightly.

One means of describing solution concentration is molarity:

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Since molarity relates the volume of the solution and the moles of solute, it allows the principles of stoichiometry to be applied to reactions in solution. A standard solution is one in which the molarity is accurately known. When a solution is diluted, only solvent is added, which means that

$$\text{Moles of solute after dilution} = \text{moles of solute before dilution}$$

which leads to the relationship

$$M_1V_1 = M_2V_2$$

Three types of equations describe reactions in solution: molecular equations, which show reactants and products as if they were molecules; complete ionic equations, in which all reactants and products that are strong electrolytes are represented as ions; and net ionic equations, in which only those solution components undergoing a change are represented. Spectator ions (those ions remaining unchanged in a reaction) are not included in the net ionic equation.

General rules concerning solubility help to predict the outcomes of precipitation reactions.

Key Terms

aqueous solution

Section 4.1

polar molecule

hydration

solubility

Section 4.2

solute

solvent

electrical conductivity

strong electrolyte

weak electrolyte

nonelectrolyte

acid

strong acid

strong base

weak acid

weak base

Section 4.3

molarity

standard solution

dilution

Section 4.5

precipitation reaction

precipitate

Section 4.6

molecular equation

complete ionic equation

spectator ions

net ionic equation

Section 4.8

acid

base

neutralization reaction
volumetric analysis
titration
stoichiometric (equivalence) point
indicator
endpoint

Section 4.9

oxidation–reduction (redox) reaction
oxidation state
oxidation
reduction
oxidizing agent (electron acceptor)
reducing agent (electron donor)

Section 4.10

half-reactions

Volumetric analysis involves the titration of a solution containing the substance to be determined. One type of volumetric analysis uses neutralization (acid–base) reactions; the unknown concentration of an acid is determined by titration with a base of known concentration (or vice versa). The point in the titration where just enough titrant has been added to react exactly with the substance being determined is called the stoichiometric (equivalence) point.

Oxidation–reduction (redox) reactions involve a transfer of electrons. One method for keeping track of electrons is to use oxidation states for atoms in compounds. A series of rules is used to assign these oxidation states. Oxidation is an increase in oxidation state (a loss of electrons). Reduction is a decrease in oxidation state (a gain of electrons). An oxidizing agent accepts electrons, and a reducing agent donates electrons.

Equations for oxidation–reduction reactions occurring in aqueous solution can be balanced using the half-reaction method, which splits a reaction into two parts (the oxidation half-reaction and the reduction half-reaction).

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Assume you have a highly magnified view of a solution of HCl that allows you to “see” the HCl. Draw this magnified view. If you dropped in a piece of magnesium, the magnesium would disappear and hydrogen gas would be released. Represent this change using symbols for the elements, and write out the balanced equation.
2. You have a solution of table salt in water. What happens to the salt concentration (increases, decreases, or stays the same) as the solution boils? Draw pictures to explain your answer.
3. You have a sugar solution (solution A) with concentration x . You pour one-fourth of this solution into a beaker, and add an equivalent volume of water (solution B).
 - a. What is the ratio of sugar in solutions A and B?
 - b. Compare the volumes of solutions A and B.
 - c. What is the ratio of the concentrations of sugar in solutions A and B?
4. You add an aqueous solution of lead nitrate to an aqueous solution of potassium iodide. Draw highly magnified views of each solution individually, and the mixed solution including any product that forms. Write the balanced equation for the reaction.
5. Order the following molecules from lowest to highest oxidation state of the nitrogen atom: HNO_3 , NH_4Cl , N_2O , NO_2 , NaNO_2 .
6. Why is it that when something gains electrons, it is said to be *reduced*? What is being reduced?
7. Consider separate aqueous solutions of HCl and H_2SO_4 with the same molar concentrations. You wish to neutralize an aqueous solution of NaOH. For which acid solution would

you need to add more volume (in milliliters) to neutralize the base?

- a. the HCl solution
 - b. the H_2SO_4 solution
 - c. You need to know the acid concentrations to answer this question.
 - d. You need to know the volume and concentration of the NaOH solution to answer this question.
 - e. c and d
- Explain.
8. Draw molecular-level pictures to differentiate between concentrated and dilute solutions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

9. Distinguish between the terms *slightly soluble* and *weak electrolyte*.
10. How would you determine experimentally whether a substance is a strong or weak electrolyte?

Exercises

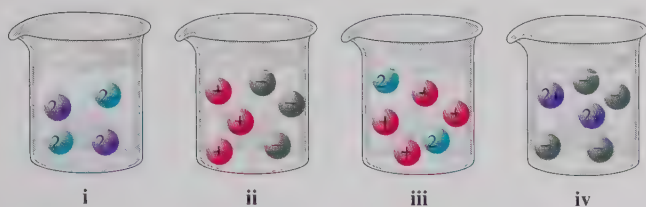
In this section similar exercises are paired.

Aqueous Solutions: Strong and Weak Electrolytes

11. Show how each of the following strong electrolytes “breaks up” into its component ions upon dissolving in water by drawing molecular-level pictures.

a. NaBr	f. FeSO_4
b. MgCl_2	g. KMnO_4
c. $\text{Al}(\text{NO}_3)_3$	h. HClO_4
d. $(\text{NH}_4)_2\text{SO}_4$	i. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate)
e. NaOH	

12. Match each name below with the following microscopic pictures of that compound in aqueous solution.



- a. barium nitrate c. potassium carbonate
b. sodium chloride d. magnesium sulfate

13. Calcium chloride is a strong electrolyte and is used to “salt” streets in the winter to melt ice and snow. Write a reaction to show how this substance breaks apart when it dissolves in water.
14. Commercial cold packs and hot packs are available for treating athletic injuries. Both types contain a pouch of water and a dry chemical. When the pack is struck, the pouch of water breaks, dissolving the chemical, and the solution becomes either hot or cold. Many hot packs use magnesium sulfate, and many cold packs use ammonium nitrate. Write reactions to show how these strong electrolytes break apart when they dissolve in water.

Solution Concentration: Molarity

15. Calculate the molarity of each of these solutions.
- A 5.623-g sample of NaHCO_3 is dissolved in enough water to make 250.0 mL of solution.
 - A 184.6-mg sample of $\text{K}_2\text{Cr}_2\text{O}_7$ is dissolved in enough water to make 500.0 mL of solution.
 - A 0.1025-g sample of copper metal is dissolved in 35 mL of concentrated HNO_3 to form Cu^{2+} ions and then water is added to make a total volume of 200.0 mL. (Calculate the molarity of Cu^{2+} .)
16. A solution of ethanol ($\text{C}_2\text{H}_5\text{OH}$) in water is prepared by dissolving 75.0 mL of ethanol (density = 0.79 g/cm^3) in enough water to make 250.0 mL of solution. What is the molarity of the ethanol in this solution?
17. Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
- 0.15 M CaCl_2
 - $0.26 \text{ M Al}(\text{NO}_3)_3$
 - $0.25 \text{ M K}_2\text{Cr}_2\text{O}_7$
 - $2.0 \times 10^{-3} \text{ M Al}_2(\text{SO}_4)_3$
18. Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
- 0.100 mol of $\text{Ca}(\text{NO}_3)_2$ in 100.0 mL of solution
 - 2.5 mol of Na_2SO_4 in 1.25 L of solution
 - 5.00 g of NH_4Cl in 500.0 mL of solution
 - 1.00 g K_3PO_4 in 250.0 mL of solution
19. Which of the following solutions of strong electrolytes contains the largest number of moles of chloride ions: 100.0 mL of 0.30 M AlCl_3 , 50.0 mL of 0.60 M MgCl_2 , or 200.0 mL of 0.40 M NaCl ?
20. Which of the following solutions of strong electrolytes contains the largest number of ions: 100.0 mL of 0.100 M NaOH , 50.0 mL of 0.200 M BaCl_2 , or 75.0 mL of $0.150 \text{ M Na}_3\text{PO}_4$?
21. What volume of a 0.100 M solution of NaHCO_3 contains 0.350 g of NaHCO_3 ?
22. How many grams of NaOH are contained in 250.0 mL of a 0.400 M sodium hydroxide solution?
23. Describe how you would prepare 2.00 L of each of the following solutions.
- 0.250 M NaOH from solid NaOH
 - 0.250 M NaOH from 1.00 M NaOH stock solution
 - $0.100 \text{ M K}_2\text{CrO}_4$ from solid K_2CrO_4
 - $0.100 \text{ M K}_2\text{CrO}_4$ from $1.75 \text{ M K}_2\text{CrO}_4$ stock solution
24. How would you prepare 1.00 L of a 0.50 M solution of each of the following?
- H_2SO_4 from “concentrated” (18 M) sulfuric acid
 - HCl from “concentrated” (12 M) reagent
 - NiCl_2 from the salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
 - HNO_3 from “concentrated” (16 M) reagent
 - Sodium carbonate from the pure solid
25. A solution is prepared by dissolving 10.8 g ammonium sulfate in enough water to make 100.0 mL of stock solution. A 10.00-mL sample of this stock solution is added to 50.00 mL of water. Calculate the concentration of ammonium ions and sulfate ions in the final solution.
26. Calculate the sodium ion concentration when 70.0 mL of 3.0 M sodium carbonate is added to 30.0 mL of 1.0 M sodium bicarbonate.
27. A standard solution is prepared for the analysis of fluoxymesterone ($\text{C}_{20}\text{H}_{29}\text{FO}_3$), an anabolic steroid. A stock solution is first prepared by dissolving 10.0 mg of fluoxymesterone in enough water to give a total volume of 500.0 mL. A $100.0\text{-}\mu\text{L}$ aliquot (portion) of this solution is diluted to a final volume of 100.0 mL. Calculate the concentration of the final solution in terms of molarity.
28. A stock solution containing Mn^{2+} ions was prepared by dissolving 1.584 g pure manganese metal in nitric acid and diluting to a final volume of 1.000 L. The following solutions were then prepared by dilution:
- For solution A, 50.00 mL of stock solution was diluted to 1000.0 mL.
- For solution B, 10.00 mL of solution A was diluted to 250.0 mL.
- For solution C, 10.00 mL of solution B was diluted to 500.0 mL.
- Calculate the concentrations of the stock solution and solutions A, B, and C.

Precipitation Reactions

29. When the following solutions are mixed together, what precipitate (if any) will form?

- $\text{BaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq)$
- $\text{Pb}(\text{NO}_3)_2(aq) + \text{KCl}(aq)$
- $\text{AgNO}_3(aq) + \text{Na}_3\text{PO}_4(aq)$
- $\text{NaOH}(aq) + \text{Fe}(\text{NO}_3)_3(aq)$

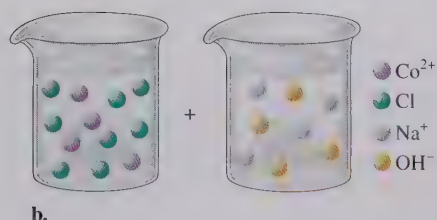
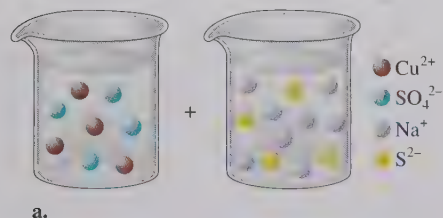
30. When the following solutions are mixed together, what precipitate (if any) will form?

- $\text{FeSO}_4(aq) + \text{KCl}(aq)$
- $\text{Al}(\text{NO}_3)_3(aq) + \text{Ba}(\text{OH})_2(aq)$
- $\text{CaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq)$
- $\text{K}_2\text{S}(aq) + \text{Ni}(\text{NO}_3)_2(aq)$

31. For the reactions in Exercise 29, write the balanced molecular equation, complete ionic equation, and net ionic equation. If no precipitate forms, write "No reaction."

32. For the reactions in Exercise 30, write the balanced molecular equation, complete ionic equation, and net ionic equation. If no precipitate forms, write "No reaction."

33. Write the balanced molecular and net ionic equation for the reaction that occurs when the contents of the two beakers are added together. What colors represent the spectator ions in each reaction?



34. Give an example how each of the following insoluble ionic compounds could be produced using a precipitation reaction. Write the balanced molecular equation for each reaction.

- $\text{Fe}(\text{OH})_3(s)$
- $\text{Hg}_2\text{Cl}_2(s)$
- $\text{PbSO}_4(s)$
- $\text{BaCrO}_4(s)$

35. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

- ammonium sulfate and barium nitrate
- lead(II) nitrate and sodium chloride
- sodium phosphate and potassium nitrate
- sodium bromide and rubidium chloride
- copper(II) chloride and sodium hydroxide

36. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

- chromium(III) chloride and sodium hydroxide
- silver nitrate and ammonium carbonate
- copper(II) sulfate and mercury(I) nitrate
- strontium nitrate and potassium iodide

37. A lake may be polluted with Pb^{2+} ions. What precipitation reaction might you use to test for the presence of Pb^{2+} ?

38. A sample may contain any or all of the following ions: Hg_2^{2+} , Ba^{2+} , and Mn^{2+} .

- No precipitate formed when an aqueous solution of NaCl was added to the sample solution.
- No precipitate formed when an aqueous solution of Na_2SO_4 was added to the sample solution.
- A precipitate formed when the sample solution was made basic with NaOH .

Which ion or ions are present in the sample solution?

39. What mass of Na_2CrO_4 is required to precipitate all of the silver ions from 75.0 mL of a 0.100 M solution of AgNO_3 ?

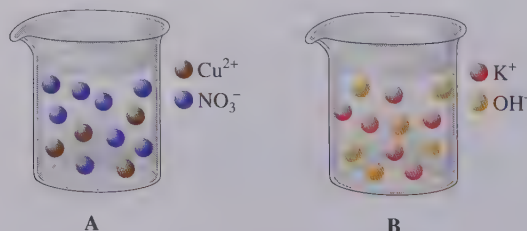
40. What volume of 0.100 M Na_3PO_4 is required to precipitate all the lead(II) ions from 150.0 mL of 0.250 M $\text{Pb}(\text{NO}_3)_2$?

41. What mass of solid aluminum hydroxide can be produced when 50.0 mL of 0.200 M $\text{Al}(\text{NO}_3)_3$ is added to 200.0 mL of 0.100 M KOH ?

42. What mass of barium sulfate can be produced when 100.0 mL of a 0.100 M solution of barium chloride is mixed with 100.0 mL of a 0.100 M solution of iron(III) sulfate?

43. How many grams of silver chloride can be prepared by the reaction of 100.0 mL of 0.20 M silver nitrate with 100.0 mL of 0.15 M calcium chloride? Calculate the concentrations of each ion remaining in solution after precipitation is complete.

44. The drawings below represent aqueous solutions. Solution A is 2.00 L of a 2.00 M aqueous solution of copper(II) nitrate. Solution B is 2.00 L of a 3.00 M aqueous solution of potassium hydroxide.



- a. Draw a picture of the solution made by mixing solutions A and B together after the precipitation reaction takes place. Make sure this picture shows the correct relative volume compared to solutions A and B, and the correct relative number of ions, along with the correct relative amount of solid formed.
- b. Determine the concentrations (in M) of all ions left in solution (from part a) and the mass of solid formed.

Acid–Base Reactions

45. Write the balanced molecular, complete ionic, and net ionic equations for each of the following acid–base reactions.
 - a. $\text{HClO}_4(aq) + \text{Mg}(\text{OH})_2(s) \rightarrow$
 - b. $\text{HCN}(aq) + \text{NaOH}(aq) \rightarrow$
 - c. $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow$
46. Write the balanced molecular, complete ionic, and net ionic equations for each of the following acid–base reactions.
 - a. $\text{HNO}_3(aq) + \text{Al}(\text{OH})_3(s) \rightarrow$
 - b. $\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{KOH}(aq) \rightarrow$
 - c. $\text{Ca}(\text{OH})_2(aq) + \text{HCl}(aq) \rightarrow$
47. Write the balanced molecular, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.
 - a. potassium hydroxide (aqueous) and nitric acid
 - b. barium hydroxide (aqueous) and hydrochloric acid
 - c. perchloric acid [$\text{HClO}_4(aq)$] and solid iron(III) hydroxide
48. Write the balanced molecular, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.
 - a. solid silver hydroxide and hydrobromic acid
 - b. aqueous strontium hydroxide and hydroiodic acid
 - c. solid chromium(III) hydroxide and nitric acid
49. What volume of each of the following acids will react completely with 50.00 mL of 0.200 M NaOH?
 - a. 0.100 M HCl
 - b. 0.150 M HNO_3
 - c. 0.200 M $\text{HC}_2\text{H}_3\text{O}_2$ (1 acidic hydrogen)
50. What volume of each of the following bases will react completely with 25.00 mL of 0.200 M HCl?
 - a. 0.100 M NaOH
 - b. 0.0500 M $\text{Ba}(\text{OH})_2$
 - c. 0.250 M KOH

51. A solution is prepared by dissolving 15.0 g NaOH in 150.0 mL of 0.250 M nitric acid. Will the final solution be acidic, basic, or neutral? Calculate the concentrations of all the ions present in the solution after the reaction has occurred. Assume no volume change on addition of NaOH.
52. Hydrochloric acid (75.0 mL of 0.250 M) is added to 225.0 mL of 0.0550 M $\text{Ba}(\text{OH})_2$ solution. What is the concentration of the excess H^+ or OH^- ions left in this solution?

53. A 25.00-mL sample of hydrochloric acid solution requires 24.16 mL of 0.106 M sodium hydroxide for complete neutralization. What is the concentration of the original hydrochloric acid solution?

54. What volume of 0.0200 M calcium hydroxide is required to neutralize 35.00 mL of 0.0500 M nitric acid?

55. A student titrates an unknown amount of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, often abbreviated KHP) with 20.46 mL of a 0.1000 M NaOH solution. KHP (molar mass = 204.22 g/mol) has one acidic hydrogen. How many grams of KHP were titrated (reacted completely) by the sodium hydroxide solution?
56. The concentration of a certain sodium hydroxide solution was determined by using the solution to titrate a sample of potassium hydrogen phthalate (abbreviated as KHP). KHP is an acid with one acidic hydrogen and a molar mass of 204.22 g/mol. In the titration, 34.67 mL of the sodium hydroxide solution was required to react with 0.1082 g KHP. Calculate the molarity of the sodium hydroxide.

Oxidation–Reduction Reactions

57. Assign oxidation states for all atoms in each of the following compounds.

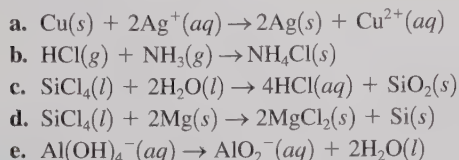
a. KMnO_4	f. Fe_3O_4
b. NiO_2	g. XeOF_4
c. $\text{K}_4\text{Fe}(\text{CN})_6$ (Fe only)	h. SF_4
d. $(\text{NH}_4)_2\text{HPO}_4$	i. CO
e. P_4O_6	j. $\text{Na}_2\text{C}_2\text{O}_4$
58. Assign oxidation states for all atoms in each of the following compounds.

a. UO_2^{2+}	f. $\text{Mg}_2\text{P}_2\text{O}_7$
b. As_2O_3	g. $\text{Na}_2\text{S}_2\text{O}_3$
c. NaBiO_3	h. Hg_2Cl_2
d. As_4	i. $\text{Ca}(\text{NO}_3)_2$
e. HAsO_2	
59. Assign the oxidation state for bromine in each of the following compounds.
 - a. HBr
 - b. HOBr
 - c. Br_2
 - d. HBrO_4
 - e. BrF_3
60. Assign the oxidation state for nitrogen in each of the following.

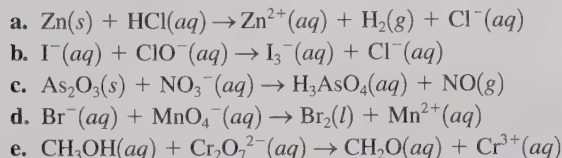
a. Li_3N	f. NO_2
b. NH_3	g. NO_2^-
c. N_2H_4	h. NO_3^-
d. NO	i. N_2
e. N_2O	

61. Specify which of the following are oxidation–reduction reactions, and identify the oxidizing agent, the reducing agent, the substance being oxidized, and the substance being reduced.
 - a. $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
 - b. $\text{Zn}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$
 - c. $\text{Cr}_2\text{O}_7^{2-}(aq) + 2\text{OH}^-(aq) \rightarrow 2\text{CrO}_4^{2-}(aq) + \text{H}_2\text{O}(l)$
 - d. $\text{O}_3(g) + \text{NO}(g) \rightarrow \text{O}_2(g) + \text{NO}_2(g)$
 - e. $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
 - f. $2\text{CuCl}(aq) \rightarrow \text{CuCl}_2(aq) + \text{Cu}(s)$

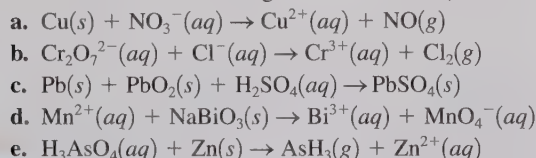
62. Specify which of the following are oxidation–reduction reactions, and identify the oxidizing agent, the reducing agent, the substance being oxidized, and the substance being reduced.



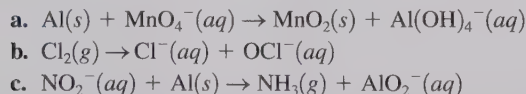
63. Balance the following oxidation–reduction reactions that occur in acidic solution.



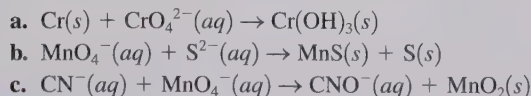
64. Balance the following oxidation–reduction reactions that occur in acidic solution using the half-reaction method.



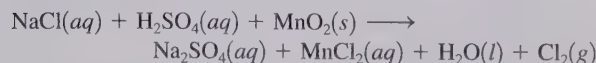
65. Balance the following oxidation–reduction reactions that occur in basic solution.



66. Balance the following oxidation–reduction reactions that occur in basic solution.



67. Chlorine gas was first prepared in 1774 by C. W. Scheele by oxidizing sodium chloride with manganese(IV) oxide. The reaction is



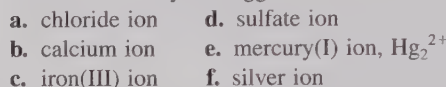
Balance this equation.

68. Gold metal will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. It will dissolve, however, in aqua regia, a mixture of the two concentrated acids. The products of the reaction are the AuCl_4^- ion and gaseous NO. Write a balanced equation for the dissolution of gold in aqua regia.

What is the molarity of hydroxide ions in the solution formed when 0.100 g calcium metal is dissolved in enough water to make a final volume of 450. mL?

70. A 230.-mL sample of a 0.275 M CaCl_2 solution is left on a hot plate overnight; the following morning, the solution is 1.10 M. What volume of water evaporated from the 0.275 M CaCl_2 solution?

71. Using the general solubility rules given in Table 4.1, name three reagents that would form precipitates with each of the following ions in aqueous solution. Write the net ionic equation for each of your suggestions.



72. Consider a 1.50-g mixture of magnesium nitrate and magnesium chloride. After dissolving this mixture in water, 0.500 M silver nitrate is added dropwise until precipitate formation is complete. The mass of the white precipitate formed is 0.641 g.

- Calculate the mass percent of magnesium chloride in the mixture.
- Determine the minimum volume of silver nitrate that must have been added to ensure complete formation of the precipitate.

73. During the developing process of black-and-white film, silver bromide is removed from photographic film by the fixer. The major component of the fixer is sodium thiosulfate. The net ionic equation for the reaction is

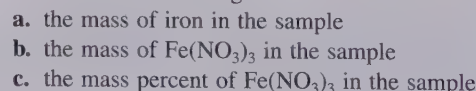


What mass of AgBr can be dissolved by 1.00 L of 0.200 M $\text{Na}_2\text{S}_2\text{O}_3$?

74. A 1.42-g sample of a pure compound, with formula M_2SO_4 , was dissolved in water and treated with an excess of aqueous calcium chloride, resulting in the precipitation of all the sulfate ions as calcium sulfate. The precipitate was collected, dried, and found to weigh 1.36 g. Determine the atomic mass of M, and identify M.

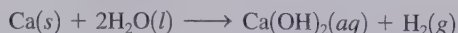
75. Saccharin ($\text{C}_7\text{H}_5\text{NO}_3\text{S}$) is sometimes dispensed in tablet form. Ten tablets with a total mass of 0.5894 g were dissolved in water. They were oxidized to convert all the sulfur to sulfate ion, which was precipitated by adding an excess of barium chloride solution. The mass of BaSO_4 obtained was 0.5032 g. What is the average mass of saccharin per tablet? What is the average mass percent of saccharin in the tablets?

76. A mixture contains only NaCl and $\text{Fe}(\text{NO}_3)_3$. A 0.456-g sample of the mixture is dissolved in water, and an excess of NaOH is added, producing a precipitate of $\text{Fe}(\text{OH})_3$. The precipitate is filtered, dried, and weighed. Its mass is 0.107 g. Calculate the following.



Additional Exercises

69. Calcium metal will react with water as follows:



77. A student added 50.0 mL of an NaOH solution to 100.0 mL of 0.400 *M* HCl. The solution was then treated with an excess of aqueous chromium(III) nitrate, resulting in formation of 2.06 g of precipitate. Determine the concentration of the NaOH solution.
78. What acid and what strong base would react in aqueous solution to produce the following salts in the molecular equation? Write the balanced molecular equation for each reaction.
- potassium perchlorate
 - cesium nitrate
 - calcium iodide
79. A 10.00-mL sample of vinegar, an aqueous solution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), is titrated with 0.5062 *M* NaOH, and 16.58 mL is required to reach the equivalence point.
- What is the molarity of the acetic acid?
 - If the density of the vinegar is 1.006 g/cm³, what is the mass percent of acetic acid in the vinegar?
80. When hydrochloric acid reacts with magnesium metal, hydrogen gas and aqueous magnesium chloride are produced. What volume of 5.0 *M* HCl is required to react completely with 3.00 g of magnesium?
81. A 2.20-g sample of an unknown acid (empirical formula = $\text{C}_3\text{H}_4\text{O}_3$) is dissolved in 1.0 L of water. A titration required 25.0 mL of 0.500 *M* NaOH to react completely with all the acid present. Assuming the unknown acid has one acidic proton per molecule, what is the molecular formula of the unknown acid?
82. Many oxidation–reduction reactions can be balanced by inspection. Try to balance the following reactions by inspection. In each reaction, identify the substance reduced and the substance oxidized.
- $\text{Al}(s) + \text{HCl}(aq) \rightarrow \text{AlCl}_3(aq) + \text{H}_2(g)$
 - $\text{CH}_4(g) + \text{S}(s) \rightarrow \text{CS}_2(l) + \text{H}_2\text{S}(g)$
 - $\text{C}_3\text{H}_8(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$
 - $\text{Cu}(s) + \text{Ag}^+(aq) \rightarrow \text{Ag}(s) + \text{Cu}^{2+}(aq)$
83. One of the classical methods for the determination of the manganese content in steel is to convert all the manganese to the deeply colored permanganate ion and then to measure the absorption of light. The steel is dissolved in nitric acid, producing the manganese(II) ion and nitrogen dioxide gas. This solution is then reacted with an acidic solution containing periodate ion; the products are the permanganate and iodate ions. Write balanced chemical equations for both these steps.

Challenge Problems

84. The units of parts per million (ppm) and parts per billion (ppb) are commonly used by environmental chemists. In general, 1 ppm means 1 part of solute for every 10⁶ parts of solution. Mathematically, by mass:

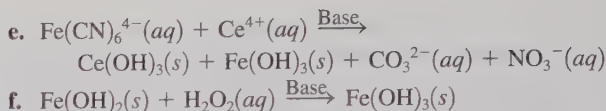
$$\text{ppm} = \frac{\mu\text{g solute}}{\text{g solution}} = \frac{\text{mg solute}}{\text{kg solution}}$$

In the case of very dilute aqueous solutions, a concentration of 1.0 ppm is equal to 1.0 μg of solute per 1.0 mL, which equals 1.0 g solution. Parts per billion is defined in a similar fashion. Calculate the molarity of each of the following aqueous solutions.

- 5.0 ppb Hg in H_2O
 - 1.0 ppb CHCl_3 in H_2O
 - 10.0 ppm As in H_2O
 - 0.10 ppm DDT ($\text{C}_{14}\text{H}_9\text{Cl}_5$) in H_2O
85. In most of its ionic compounds, cobalt is either Co(II) or Co(III). One such compound, containing chloride ion and waters of hydration, was analyzed, and the following results were obtained. A 0.256-g sample of the compound was dissolved in water, and excess silver nitrate was added. The silver chloride was filtered, dried, and weighed, and it had a mass of 0.308 g. A second sample of 0.416 g of the compound was dissolved in water, and an excess of sodium hydroxide was added. The hydroxide salt was filtered and heated in a flame, forming cobalt(III) oxide. The mass of cobalt(III) oxide formed was 0.145 g.
- What is the percent composition, by mass, of the compound?
 - Assuming the compound contains one cobalt atom per formula unit, what is the molecular formula?
 - Write balanced equations for the three reactions described.
86. Polychlorinated biphenyls (PCBs) have been used extensively as dielectric materials in electrical transformers. Because PCBs have been shown to be potentially harmful, analysis for their presence in the environment has become very important. PCBs are manufactured according to the following generic reaction:
- $$\text{C}_{12}\text{H}_{10} + n\text{Cl}_2 \rightarrow \text{C}_{12}\text{H}_{10-n}\text{Cl}_n + n\text{HCl}$$
- This reaction results in a mixture of PCB products. The mixture is analyzed by decomposing the PCBs and then precipitating the resulting Cl^- as AgCl .
- Develop a general equation that relates the average value of *n* to the mass of a given mixture of PCBs and the mass of AgCl produced.
 - A 0.1947-g sample of a commercial PCB yielded 0.4791 g of AgCl . What is the average value of *n* for this sample?
87. You have two 500.0 mL aqueous solutions. Solution A is a solution of silver nitrate, and solution B is a solution of potassium chromate. The masses of the solutes in each of the solutions are the same. When the solutions are added together, a blood-red precipitate forms. After the reaction has gone to completion, you dry the solid and find that it has a mass of 331.8 g.
- Calculate the concentration of the potassium ions in the original potassium chromate solution.
 - Calculate the concentration of the chromate ions in the final solution.
88. A sample is a mixture of KCl and KBr. When 0.1024 g of the sample is dissolved in water and reacted with excess silver

nitrate, 0.1889 g solid is obtained. What is the composition by mass percent of the original mixture?

89. You are given a solid that is a mixture of Na_2SO_4 and K_2SO_4 . A 0.205-g sample of the mixture is dissolved in water. An excess of an aqueous solution of BaCl_2 is added. The BaSO_4 that is formed is filtered, dried, and weighed. Its mass is 0.298 g. What mass of SO_4^{2-} ion is in the sample? What is the mass percent of SO_4^{2-} ion in the sample? What are the percent compositions by mass of Na_2SO_4 and K_2SO_4 in the sample?
90. Complete and balance each acid–base reaction.
- $\text{H}_3\text{PO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
Contains three acidic hydrogens
 - $\text{H}_2\text{SO}_4(\text{aq}) + \text{Al}(\text{OH})_3(\text{s}) \rightarrow$
Contains two acidic hydrogens
 - $\text{H}_2\text{Se}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow$
Contains two acidic hydrogens
 - $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
Contains two acidic hydrogens
91. What volume of 0.0521 M $\text{Ba}(\text{OH})_2$ is required to neutralize exactly 14.20 mL of 0.141 M H_3PO_4 ? Phosphoric acid contains three acidic hydrogens.
92. A 10.00-mL sample of sulfuric acid from an automobile battery requires 35.08 mL of 2.12 M sodium hydroxide solution for complete neutralization. What is the molarity of the sulfuric acid? Sulfuric acid contains two acidic hydrogens.
93. Some of the substances commonly used in stomach antacids are MgO , $\text{Mg}(\text{OH})_2$, and $\text{Al}(\text{OH})_3$.
- Write a balanced equation for the neutralization of hydrochloric acid by each of these substances.
 - Which of these substances will neutralize the greatest amount of 0.10 M HCl per gram?
94. Carminic acid, a naturally occurring red pigment extracted from the cochineal insect, contains only carbon, hydrogen, and oxygen. It was commonly used as a dye in the first half of the nineteenth century. It is 53.66% C and 4.09% H by mass. A titration required 18.02 mL of 0.0406 M NaOH to neutralize 0.3602 g carminic acid. Assuming that there is only one acidic hydrogen per molecule, what is the molecular formula of carminic acid?
95. Citric acid, which can be obtained from lemon juice, has the molecular formula $\text{C}_6\text{H}_8\text{O}_7$. A 0.250-g sample of citric acid dissolved in 25.0 mL of water requires 37.2 mL of 0.105 M NaOH for complete neutralization. How many acidic hydrogens per molecule does citric acid have?
96. Balance the following equations by the half-reaction method.
- $\text{Fe}(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{HFeCl}_4(\text{aq}) + \text{H}_2(\text{g})$
 - $\text{IO}_3^-(\text{aq}) + \text{I}^-(\text{aq}) \xrightarrow{\text{Acid}} \text{I}_3^-(\text{aq})$
 - $\text{Cr}(\text{NCS})_6^{4-}(\text{aq}) + \text{Ce}^{4+}(\text{aq}) \xrightarrow{\text{Acid}} \text{Cr}^{3+}(\text{aq}) + \text{Ce}^{3+}(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{CO}_2(\text{g}) + \text{SO}_4^{2-}(\text{aq})$
 - $\text{CrI}_3(\text{s}) + \text{Cl}_2(\text{g}) \xrightarrow{\text{Base}} \text{CrO}_4^{2-}(\text{aq}) + \text{IO}_4^-(\text{aq}) + \text{Cl}^-(\text{aq})$



97. It took 25.06 ± 0.05 mL of a sodium hydroxide solution to titrate a 0.4016-g sample of KHP (see Exercise 55). Calculate the concentration and uncertainty in the concentration of the sodium hydroxide solution. (See Appendix 1.5.) Neglect any uncertainty in the mass.

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

98. Three students were asked to find the identity of the metal in a particular sulfate salt. They dissolved a 0.1472-g sample of the salt in water and treated it with excess barium chloride, resulting in the precipitation of barium sulfate. After the precipitate had been filtered and dried, it weighed 0.2327 g.

Each student analyzed the data independently and came to different conclusions. Pat decided that the metal was titanium. Chris thought it was sodium. Randy reported that it was gallium. What formula did each student assign to the sulfate salt?

Look for information on the sulfates of gallium, sodium, and titanium in this text and reference books such as the *CRC Handbook of Chemistry and Physics*. What further tests would you suggest to determine which student is most likely correct?



Media Activities

- Play the Dissolution of a Solid in a Liquid CD Visualization on the student CD, which shows the hydration process for NaCl .
 - Which color sphere represents the Na^+ ions?
 - Which color represents the Cl^- ions?
 - Is $\text{NaCl}(\text{aq})$ a strong, weak, or nonelectrolyte? Explain the differences between the various types of electrolytes.
- Open the Conductivities of Aqueous Solutions Visualization and play the demonstration illustrating the differences in conductivity between strong, weak, and nonelectrolytes in water. In the demo, nothing happened to the light when distilled water was used, the bulb was very dimly lit for sparkling mineral water, the bulb was slightly brighter for the soft drinks tested, and was brightest when $\text{HCl}(\text{aq})$ was tested.
 - Explain these results.
 - What would you expect to happen if sugar water [$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$] was tested?
 - Finally, which compounds are generally classified as strong electrolytes? As weak electrolytes? As nonelectrolytes?

Make sure you understand the illustrations in Figures 4.5–4.9 in the text, which show the differences between the types of electrolytes.

3. Open the Precipitation Reactions Understanding Concepts activity on the Student CD and go through the introduction and example. The animation of the silver chloride is important to understand.
 - a. What is the blue ball in the animation?
 - b. What ion is missing from the animation?
 - c. Consider the reaction between 4 formula units of $\text{Pb}(\text{NO}_3)_2(\text{aq})$ and 3 formula units of $\text{CaCl}_2(\text{aq})$. After precipitate formation is complete, how many and which type of ions remain in solution? Which ion is the limiting reactant in this reaction? Understanding atomic level views of precipitation reactions is extremely important. Drawing a picture is often helpful.
4. In the simplest form, acid–base reactions involve the transfer of a proton (H^+) from an acid to a base. When the base contains OH^- ions, the H^+ from the acid reacts with OH^- to form H_2O (we commonly say that the added OH^- neutralizes the acid). In real life, acid–base reactions are more complicated than this and are discussed in more detail in Chapters 14 and 15 of the text. To see an advanced look at acid–base reactions, open the Acid/Base Understanding Concepts activity on the student CD. Note that this activity goes into more detail than the ideas presented on acid–base reactions in Chapter 4 of the text.
5. Oxidation–reduction reactions are another common type of aqueous reactions. Open the Oxidation–Reduction Reactions Understanding Concepts activity on the student CD and go through the introduction to review pertinent ideas. In the animation, what color sphere represents tin? Zinc? What are the green balls? Do the Example and Exercises only if your class has discussed the activity series.
6. Open the Zinc and Iodine Visualization and play the demo to see an energetic oxidation–reduction. The product of the reaction is zinc iodide. With this in mind, what is oxidized? What is reduced? What is the oxidizing agent? What is the reducing agent?
7. Test your understanding of Chapter 4 by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



BREITLING
ORBITER 3

Gases

5

Matter exists in three distinct physical states: gas, liquid, and solid. Although relatively few substances exist in the gaseous state under typical conditions, gases are very important. For example, we live immersed in a gaseous solution. The earth's atmosphere is a mixture of gases that consists mainly of elemental nitrogen (N_2) and oxygen (O_2). The atmosphere both supports life and acts as a waste receptacle for the exhaust gases that accompany many industrial processes. The chemical reactions of these waste gases in the atmosphere lead to various types of pollution, including smog and acid rain. The gases in the atmosphere also shield us from harmful radiation from the sun and keep the earth warm by reflecting heat radiation back toward the earth. In fact, there is now great concern that an increase in atmospheric carbon dioxide, a product of the combustion of fossil fuels, is causing a dangerous warming of the earth.

In this chapter we will look carefully at the properties of gases. First we will see how measurements of gas properties lead to various types of laws—statements that show how the properties are related to each other. Then we will construct a model to explain why gases behave as they do. This model will show how the behavior of the individual particles of a gas leads to the observed properties of the gas itself (a collection of many, many particles).

The study of gases provides an excellent example of the scientific method in action. It illustrates how observations lead to natural laws, which in turn can be accounted for by models.

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- 5.1 Pressure**
 - Units of Pressure
- 5.2 The Gas Laws of Boyle, Charles, and Avogadro**
 - Boyle's Law
 - Charles's Law
 - Avogadro's Law
- 5.3 The Ideal Gas Law**
- 5.4 Gas Stoichiometry**
 - Molar Mass of a Gas
- 5.5 Dalton's Law of Partial Pressures**
- 5.6 The Kinetic Molecular Theory of Gases**
 - Pressure and Volume (Boyle's Law)
 - Pressure and Temperature
 - Volume and Temperature (Charles's Law)
 - Volume and Number of Moles (Avogadro's Law)
 - Mixture of Gases (Dalton's Law)
 - Deriving the Ideal Gas Law
 - The Meaning of Temperature
 - Root Mean Square Velocity
- 5.7 Effusion and Diffusion**
 - Effusion
 - Diffusion
- 5.8 Real Gases**
- 5.9 Chemistry in the Atmosphere**

The Breitling Orbiter 3, shown over the Swiss Alps, recently completed a nonstop trip around the world.

5.1 Pressure

A gas uniformly fills any container, is easily compressed, and mixes completely with any other gas. One of the most obvious properties of a gas is that it exerts pressure on its surroundings. For example, when you blow up a balloon, the air inside pushes against the elastic sides of the balloon and keeps it firm.

As mentioned earlier, the gases most familiar to us form the earth's atmosphere. The pressure exerted by this gaseous mixture that we call air can be dramatically demonstrated by the experiment shown in Fig. 5.1. A small volume of water is placed in a metal can, and the water is boiled, which fills the can with steam. The can is then sealed and allowed to cool. Why does the can collapse as it cools? It is the atmospheric pressure that crumples the can. When the can is cooled after being sealed so that no air can flow in, the water vapor (steam) condenses to a very small volume of liquid water. As a gas, the water filled the can, but when it is condensed to a liquid, the liquid does not come close to filling the can. The H_2O molecules formerly present as a gas are now collected in a very small volume of liquid, and there are very few molecules of gas left to exert pressure outward and counteract the air pressure. As a result, the pressure exerted by the gas molecules in the atmosphere smashes the can.

A device to measure atmospheric pressure, the **barometer**, was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608–1647), who had been a student of Galileo. Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury, as shown in Fig. 5.2. Notice that a large quantity of mercury stays in the tube. In fact, at sea level the height of this column of mercury averages 760 mm. Why does this mercury stay in the tube, seemingly in defiance of gravity? Figure 5.2 illustrates how the pressure exerted by the atmospheric gases on the surface of mercury in the dish keeps the mercury in the tube.

Atmospheric pressure results from the mass of the air being pulled toward the center of the earth by gravity—in other words, it results from the weight of the air. Changing weather conditions cause the atmospheric pressure to vary, so the height

As a gas, water occupies 1200 times as much space as it does as a liquid at 25°C and atmospheric pressure.

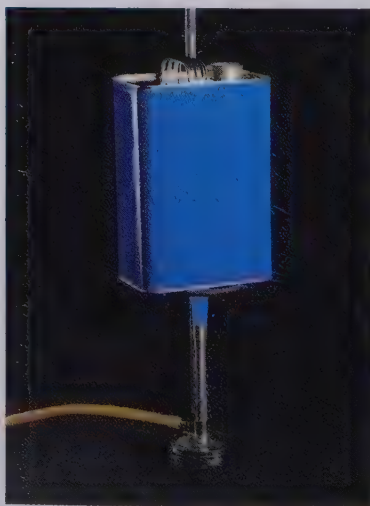
Soon after Torricelli died, a German physicist named Otto von Guericke invented an air pump. In a famous demonstration for the King of Prussia in 1663, Guericke placed two hemispheres together, pumped the air out of the resulting sphere through a valve, and showed that teams of horses could not pull the hemispheres apart. Then, after secretly opening the air valve, Guericke easily separated the hemispheres by hand. The King of Prussia was so impressed that he awarded Guericke a lifetime pension!

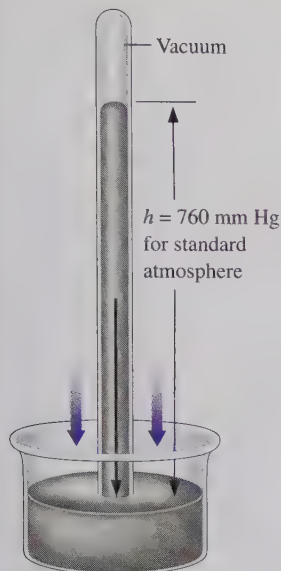


Visualization: Collapsing Can

FIGURE 5.1

The pressure exerted by the gases in the atmosphere can be demonstrated by boiling water in a large metal can (a) and then turning off the heat and sealing the can. As the can cools, the water vapor condenses, lowering the gas pressure inside the can. This causes the can to crumple (b).



**FIGURE 5.2**

A torricellian barometer. The tube, completely filled with mercury, is inverted in a dish of mercury. Mercury flows out of the tube until the pressure of the column of mercury (shown by the black arrow) “standing on the surface” of the mercury in the dish is equal to the pressure of the air (shown by the yellow arrows) on the rest of the surface of the mercury in the dish.

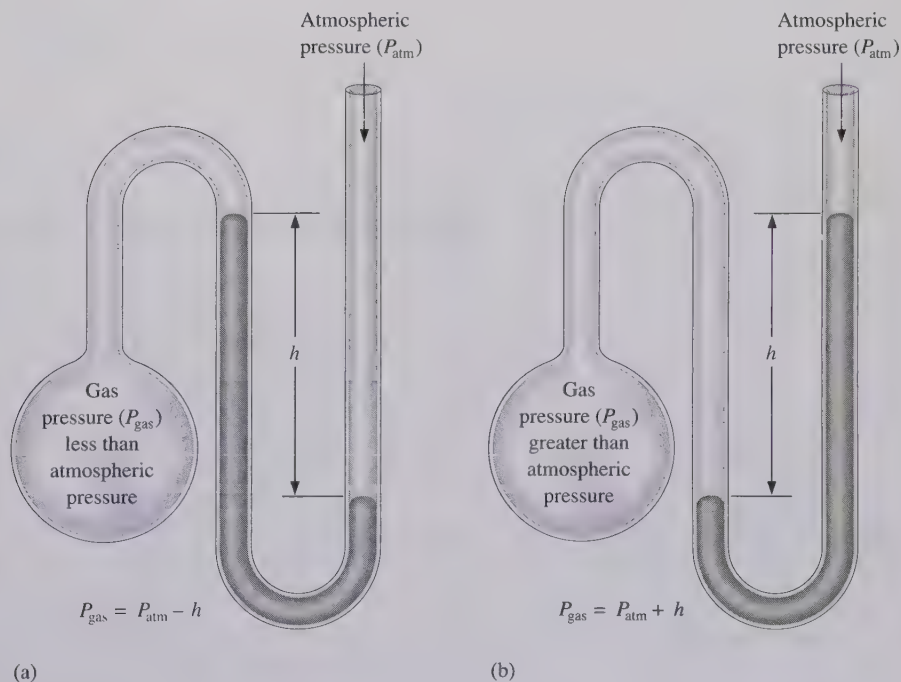
of the column of Hg supported by the atmosphere at sea level varies; it is not always 760 mm. The meteorologist who says a “low” is approaching means that the atmospheric pressure is going to decrease. This condition often occurs in conjunction with a storm.

Atmospheric pressure also varies with altitude. For example, when Torricelli’s experiment is done in Breckenridge, Colorado (elevation 9600 feet), the atmosphere supports a column of mercury only about 520 mm high because the air is “thinner.” That is, there is less air pushing down on the earth’s surface at Breckenridge than at sea level.

Units of Pressure

Because instruments used for measuring pressure, such as the **manometer** (Fig. 5.3), often contain mercury, the most commonly used units for pressure are based on the height of the mercury column (in millimeters) that the gas pressure can support. The unit **mm Hg** (millimeter of mercury) is often called the **torr** in honor of Torricelli. The terms *torr* and *mm Hg* are used interchangeably by chemists. A related unit for pressure is the **standard atmosphere** (abbreviated atm):

$$1 \text{ standard atmosphere} = 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

**FIGURE 5.3**

A simple manometer, a device for measuring the pressure of a gas in a container. The pressure of the gas is given by h (the difference in mercury levels) in units of torr (equivalent to mm Hg). (a) Gas pressure = atmospheric pressure $- h$. (b) Gas pressure = atmospheric pressure $+ h$.



Checking tire pressure.

SAMPLE EXERCISE 5.1

$$\begin{aligned}
 1 \text{ atm} &= 760 \text{ mm Hg} \\
 &= 760 \text{ torr} \\
 &= 101,325 \text{ Pa} \\
 &= 29.92 \text{ in Hg} \\
 &= 14.7 \text{ lb/in}^2
 \end{aligned}$$

However, since pressure is defined as force per unit area,

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

the fundamental units of pressure involve units of force divided by units of area. In the SI system, the unit of force is the newton (N) and the unit of area is meters squared (m^2). (For a review of the SI system, see Chapter 1.) Thus the unit of pressure in the SI system is newtons per meter squared (N/m^2) and is called the **pascal** (Pa). In terms of pascals, the standard atmosphere is

$$1 \text{ standard atmosphere} = 101,325 \text{ Pa}$$

Thus 1 atmosphere is about 10^5 pascals. Since the pascal is so small, and since it is not commonly used in the United States, we will use it sparingly in this book. However, converting from torrs or atmospheres to pascals is straightforward, as shown in Sample Exercise 5.1.

Pressure Conversions

The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals.

SOLUTION

$$\begin{aligned}
 49 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} &= 6.4 \times 10^{-2} \text{ atm} \\
 6.4 \times 10^{-2} \text{ atm} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} &= 6.5 \times 10^3 \text{ Pa}
 \end{aligned}$$

See Exercises 5.25 and 5.26.

5.2 The Gas Laws of Boyle, Charles, and Avogadro

In this section we will consider several mathematical laws that relate the properties of gases. These laws derive from experiments involving careful measurements of the relevant gas properties. From these experimental results, the mathematical relationships among the properties can be discovered. These relationships are often represented pictorially by means of graphs (plots).

We will take a historical approach to these laws to give you some perspective on the scientific method in action.



Visualization: Boyle's Law

Boyle's Law

The first quantitative experiments on gases were performed by an Irish chemist, Robert Boyle (1627–1691). Using a J-shaped tube closed at one end (Fig. 5.4), which he reportedly set up in the multistory entryway of his house, Boyle studied the relationship between the pressure of the trapped gas and its volume. Representative values from Boyle's experiments are given in Table 5.1. These data show that the product of the pressure and volume for the trapped air sample is constant within the accuracies of Boyle's measurements (note the third column in Table 5.1). This behavior can be represented by the equation

$$PV = k$$

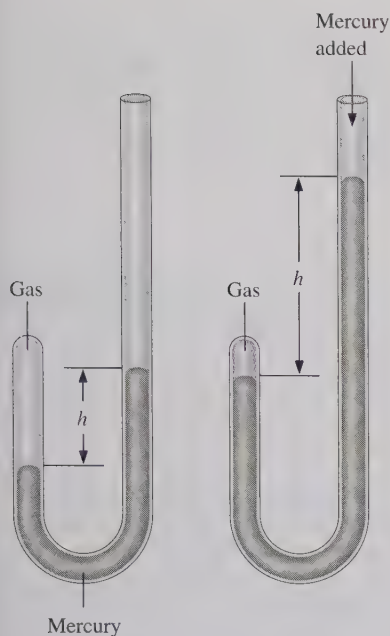


FIGURE 5.4
A J-tube similar to the one used by Boyle.

TABLE 5.1 Actual Data from Boyle's Experiment

Volume (in ³)	Pressure (in Hg)	Pressure $\times$ Volume (in Hg $\times$ in ³)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

which is called **Boyle's law** and where k is a constant for a given sample of air at a specific temperature.

It is convenient to represent the data in Table 5.1 by using two different plots. The first type of plot, P versus V , forms a curve called a *hyperbola* shown in Fig. 5.5(a). Looking at this plot, note that as the volume drops by about half (from 58.8 to 29.1), the pressure doubles (from 24.0 to 48.0). In other words, there is an *inverse relationship* between pressure and volume. The second type of plot can be obtained by rearranging Boyle's law to give

$$V = \frac{k}{P} = k \frac{1}{P}$$

which is the equation for a straight line of the type

$$y = mx + b$$

where m represents the slope and b the intercept of the straight line. In this case, $y = V$, $x = 1/P$, $m = k$, and $b = 0$. Thus a plot of V versus $1/P$ using Boyle's data gives a straight line with an intercept of zero, as shown in Fig. 5.5(b).

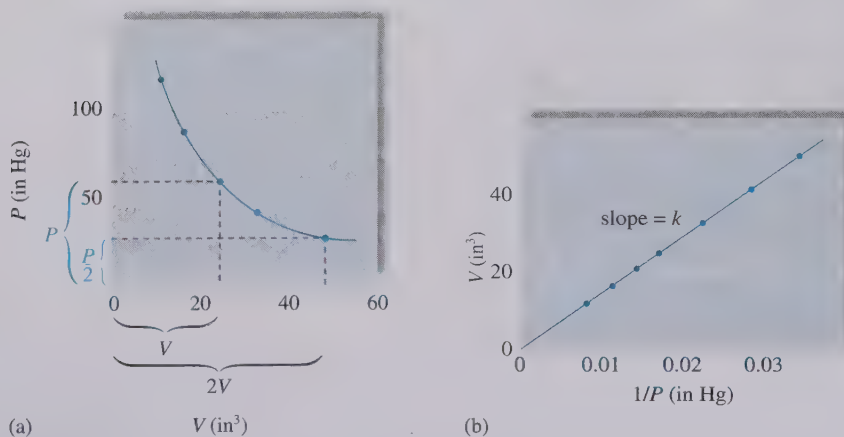
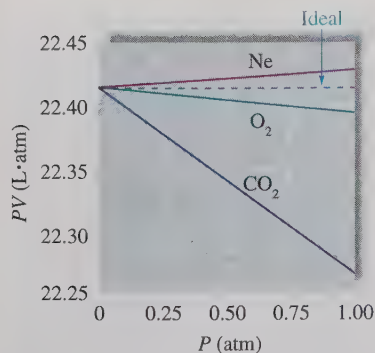


FIGURE 5.5

Plotting Boyle's data from Table 5.1. (a) A plot of P versus V shows that the volume doubles as the pressure is halved. (b) A plot of V versus $1/P$ gives a straight line. The slope of this line equals the value of the constant k .



Boyle's law: $V \propto 1/P$ at constant temperature.

Graphing is reviewed in Appendix 1.3.

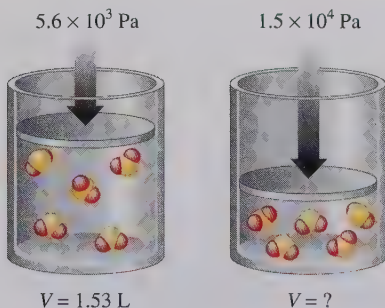
FIGURE 5.6

A plot of PV versus P for several gases at pressures below 1 atm. An ideal gas is expected to have a constant value of PV , as shown by the dotted line. Carbon dioxide shows the largest change in PV , and this change is actually quite small: PV changes from about $22.39 \text{ L} \cdot \text{atm}$ at 0.25 atm to $22.26 \text{ L} \cdot \text{atm}$ at 1.00 atm . Thus Boyle's law is a good approximation at these relatively low pressures.

In the three centuries since Boyle carried out his studies, the sophistication of measuring techniques has increased tremendously. The results of highly accurate measurements show that Boyle's law holds precisely only at very low pressures. Measurements at higher pressures reveal that PV is not constant but varies as the pressure is varied. Results for several gases at pressures below 1 atm are shown in Fig. 5.6. Note the very small changes that occur in the product PV as the pressure is changed at these low pressures. Such changes become more significant at much higher pressures, where the complex nature of the dependence of PV on pressure becomes more obvious. We will discuss these deviations and the reasons for them in detail in Section 5.8. A gas that strictly obeys Boyle's law is called an *ideal gas*. We will describe the characteristics of an ideal gas more completely in Section 5.3.

One common use of Boyle's law is to predict the new volume of a gas when the pressure is changed (at constant temperature), or vice versa. Because deviations from Boyle's law are so slight at pressures close to 1 atm, in our calculations we will assume that gases obey Boyle's law (unless stated otherwise).

SAMPLE EXERCISE 5.2



As pressure increases, the volume of SO_2 decreases.

Boyle's Law I

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53-L sample of gaseous SO_2 at a pressure of $5.6 \times 10^3 \text{ Pa}$. If the pressure is changed to $1.5 \times 10^4 \text{ Pa}$ at a constant temperature, what will be the new volume of the gas?

SOLUTION

We can solve this problem using Boyle's law,

$$PV = k$$

which also can be written as

$$P_1V_1 = k = P_2V_2 \quad \text{or} \quad P_1V_1 = P_2V_2$$

where the subscripts 1 and 2 represent two states (conditions) of the gas (both at the same temperature). In this case,

$$\begin{array}{ll} P_1 = 5.6 \times 10^3 \text{ Pa} & P_2 = 1.5 \times 10^4 \text{ Pa} \\ V_1 = 1.53 \text{ L} & V_2 = ? \end{array}$$

We can solve the preceding equation for V_2 :

$$V_2 = \frac{P_1V_1}{P_2} = \frac{5.6 \times 10^3 \text{ Pa} \times 1.53 \text{ L}}{1.5 \times 10^4 \text{ Pa}} = 0.57 \text{ L}$$

The new volume will be 0.57 L .

Boyle's law also can be written as

$$P_1V_1 = P_2V_2$$

See Exercise 5.31.

Always check that your answer makes physical (common!) sense.

The fact that the volume decreases in Sample Exercise 5.2 makes sense because the pressure was increased. *To help eliminate errors, make it a habit to check whether an answer to a problem makes physical sense.*

We mentioned before that Boyle's law is only approximately true for real gases. To determine the significance of the deviations, studies of the effect of changing pressure on the volume of a gas are often done, as shown in Sample Exercise 5.3.

SAMPLE EXERCISE 5.3

Boyle's Law II

In a study to see how closely gaseous ammonia obeys Boyle's law, several volume measurements were made at various pressures, using 1.0 mol NH_3 gas at a temperature of 0°C . Using the results listed below, calculate the Boyle's law constant for NH_3 at the various pressures.

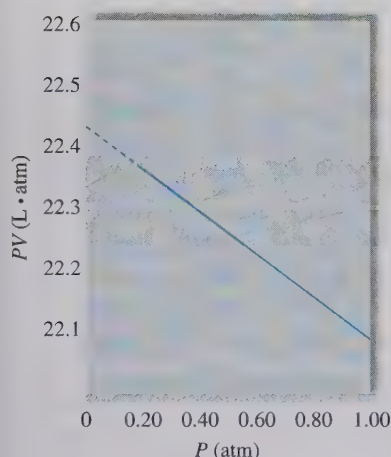


FIGURE 5.7

A plot of PV versus P for 1 mol of ammonia. The dashed line shows the extrapolation of the data to zero pressure to give the "ideal" value of PV of $22.41 \text{ L} \cdot \text{atm}$.

Experiment	Pressure (atm)	Volume (L)
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

SOLUTION

To determine how closely NH_3 gas follows Boyle's law under these conditions, we calculate the value of k (in $\text{L} \cdot \text{atm}$) for each set of values:

Experiment	1	2	3	4	5	6
$k = PV$	22.37	22.32	22.31	22.25	22.16	22.08

Although the deviations from true Boyle's law behavior are quite small at these low pressures, note that the value of k changes regularly in one direction as the pressure is increased. Thus, to calculate the "ideal" value of k for NH_3 , we can plot PV versus P , as shown in Fig. 5.7, and extrapolate (extend the line beyond the experimental points) back to zero pressure, where, for reasons we will discuss later, a gas behaves most ideally. The value of k obtained by this extrapolation is $22.41 \text{ L} \cdot \text{atm}$. Notice that this is the same value obtained from similar plots for the gases CO_2 , O_2 , and Ne at 0°C , as shown in Fig. 5.6.

Charles's Law

In the century following Boyle's findings, scientists continued to study the properties of gases. One of these scientists was a French physicist, Jacques Charles (1746–1823), who was the first person to fill a balloon with hydrogen gas and who made the first solo balloon flight. Charles found in 1787 that the volume of a gas at constant pressure increases *linearly* with the temperature of the gas. That is, a plot of



Visualization: Liquid Nitrogen and Balloons



Visualization: Charles's Law

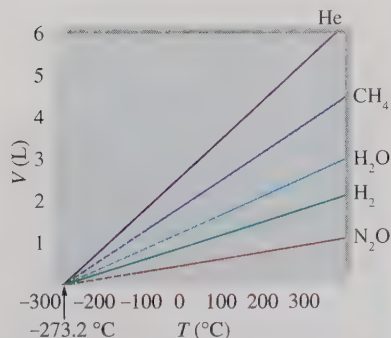


FIGURE 5.8

Plots of V versus T ($^{\circ}\text{C}$) for several gases. The solid lines represent experimental measurements on gases. The dashed lines represent extrapolation of the data into regions where these gases would become liquids or solids. Note that the samples of the various gases contain different numbers of moles.

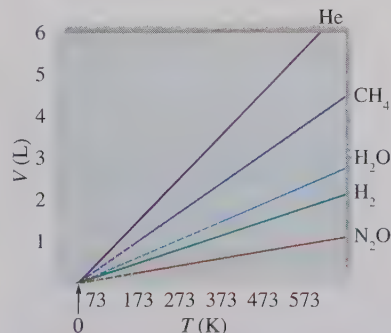


FIGURE 5.9

Plots of V versus T as in Fig. 5.8, except here the Kelvin scale is used for temperature.

Charles's law: $V \propto T$ (expressed in K) of constant pressure.

SAMPLE EXERCISE 5.4



A snowmaking machine, in which water is blown through nozzles by compressed air. The mixture is cooled by expansion to form ice crystals of snow.

the volume of a gas (at constant pressure) versus its temperature ($^{\circ}\text{C}$) gives a straight line. This behavior is shown for samples of several gases in Fig. 5.8. The slopes of the lines in this graph are different because the samples contain different numbers of moles of gas. A very interesting feature of these plots is that the volumes of all the gases extrapolate to zero at the same temperature, -273.2°C . On the Kelvin temperature scale this point is defined as 0 K, which leads to the following relationship between the Kelvin and Celsius scales:

$$\text{K} = ^{\circ}\text{C} + 273$$

When the volumes of the gases shown in Fig. 5.8 are plotted versus temperature on the Kelvin scale, the plots in Fig. 5.9 result. In this case, the volume of each gas is *directly proportional to temperature* and extrapolates to zero when the temperature is 0 K. This behavior is represented by the equation known as **Charles's law**,

$$V = bT$$

where T is in Kelvins and b is a proportionality constant.

Before we illustrate the uses of Charles's law, let us consider the importance of 0 K. At temperatures below this point, the extrapolated volumes would become negative. The fact that a gas cannot have a negative volume suggests that 0 K has a special significance. In fact, 0 K is called **absolute zero**, and there is much evidence to suggest that this temperature cannot be attained. Temperatures of approximately 0.000001 K have been produced in laboratories, but 0 K has never been reached.

Charles's Law

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

SOLUTION

Charles's law, which describes the dependence of the volume of a gas on temperature at constant pressure, can be used to solve this problem. Charles's law in the form $V = bT$ can be rearranged to

Charles's law also can be written as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

An equivalent statement is

$$\frac{V_1}{T_1} = b = \frac{V_2}{T_2}$$

where the subscripts 1 and 2 represent two states for a given sample of gas at constant pressure. In this case, we are given the following (note that the temperature values *must* be changed to the Kelvin scale):

$$\begin{array}{ll} T_1 = 15^\circ\text{C} + 273 = 288 \text{ K} & T_2 = 38^\circ\text{C} + 273 = 311 \text{ K} \\ V_1 = 2.58 \text{ L} & V_2 = ? \end{array}$$

Solving for V_2 gives

$$V_2 = \left(\frac{T_2}{T_1}\right) V_1 = \left(\frac{311 \text{ K}}{288 \text{ K}}\right) 2.58 \text{ L} = 2.79 \text{ L}$$

CHECK:

The new volume is greater than the initial volume, which makes physical sense because the gas will expand as it is heated.

See Exercise 5.32.

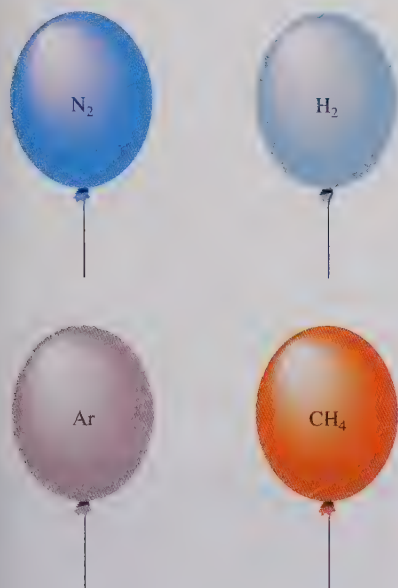


FIGURE 5.10

These balloons each hold 1.0 L of gas at 25°C and 1 atm. Each balloon contains 0.041 mol of gas, or 2.5×10^{22} molecules.

Avogadro's Law

In Chapter 2 we noted that in 1811 the Italian chemist Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of "particles." This observation is called **Avogadro's law**, which is illustrated by Fig. 5.10. Stated mathematically, Avogadro's law is

$$V = an$$

where V is the volume of the gas, n is the number of moles of gas particles, and a is a proportionality constant. This equation states that *for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas*. This relationship is obeyed closely by gases at low pressures.

SAMPLE EXERCISE 5.5

Avogadro's Law

Suppose we have a 12.2-L sample containing 0.50 mol oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25°C . If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

SOLUTION

The balanced equation for the reaction is



To calculate the moles of O_3 produced, we must use the appropriate mole ratio:

$$0.50 \text{ mol } \text{O}_2 \times \frac{2 \text{ mol } \text{O}_3}{3 \text{ mol } \text{O}_2} = 0.33 \text{ mol } \text{O}_3$$

Avogadro's law states that $V = an$, which can be rearranged to give

$$\frac{V}{n} = a$$

Avogadro's law also can be written as

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Since a is a constant, an alternative representation is

$$\frac{V_1}{n_1} = a = \frac{V_2}{n_2}$$

where V_1 is the volume of n_1 moles of O_2 gas and V_2 is the volume of n_2 moles of O_3 gas. In this case we have

$$\begin{array}{ll} n_1 = 0.50 \text{ mol} & n_2 = 0.33 \text{ mol} \\ V_1 = 12.2 \text{ L} & V_2 = ? \end{array}$$

Solving for V_2 gives

$$V_2 = \left(\frac{n_2}{n_1} \right) V_1 = \left(\frac{0.33 \text{ mol}}{0.50 \text{ mol}} \right) 12.2 \text{ L} = 8.1 \text{ L}$$

CHECK:

Note that the volume decreases, as it should, since fewer moles of gas molecules will be present after O_2 is converted to O_3 .

See Exercises 5.33 and 5.34.



Visualization: The Ideal Gas Law,
 $PV = nRT$

5.3 The Ideal Gas Law

We have considered three laws that describe the behavior of gases as revealed by experimental observations:

$$\text{Boyle's law:} \quad V = \frac{k}{P} \quad (\text{at constant } T \text{ and } n)$$

$$\text{Charles's law:} \quad V = bT \quad (\text{at constant } P \text{ and } n)$$

$$\text{Avogadro's law:} \quad V = an \quad (\text{at constant } T \text{ and } P)$$

These relationships, which show how the volume of a gas depends on pressure, temperature, and number of moles of gas present, can be combined as follows:

$$V = R \left(\frac{Tn}{P} \right)$$

where R is the combined proportionality constant called the **universal gas constant**. When the pressure is expressed in atmospheres and the volume in liters, R has the value $0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$. The preceding equation can be rearranged to the more familiar form of the **ideal gas law**:

$$PV = nRT$$

The ideal gas law is an *equation of state* for a gas, where the state of the gas is its condition at a given time. A particular *state* of a gas is described by its pressure, volume, temperature, and number of moles. Knowledge of any three of these

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

The ideal gas law applies best at pressures smaller than 1 atm.

properties is enough to completely define the state of a gas, since the fourth property can then be determined from the equation for the ideal gas law.

It is important to recognize that the ideal gas law is an empirical equation—it is based on experimental measurements of the properties of gases. A gas that obeys this equation is said to behave *ideally*. The ideal gas equation is best regarded as a limiting law—it expresses behavior that real gases *approach* at low pressures and high temperatures. Therefore, an ideal gas is a hypothetical substance. However, most gases obey the ideal gas equation closely enough at pressures below 1 atm that only minimal errors result from assuming ideal behavior. Unless you are given information to the contrary, you should assume ideal gas behavior when solving problems involving gases in this text.

The ideal gas law can be used to solve a variety of problems. Sample Exercise 5.6 demonstrates one type, where you are asked to find one property characterizing the state of a gas, given the other three.

SAMPLE EXERCISE 5.6

Ideal Gas Law I

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0°C and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.

SOLUTION

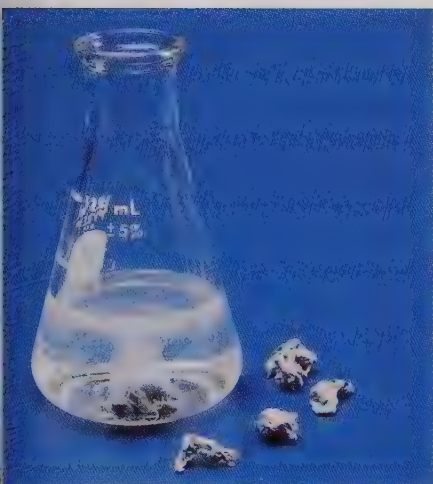
Solving the ideal gas law for n gives

$$n = \frac{PV}{RT}$$

In this case $P = 1.5 \text{ atm}$, $V = 8.56 \text{ L}$, $T = 0^\circ\text{C} + 273 = 273 \text{ K}$, and $R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$. Thus

$$n = \frac{(1.5 \text{ atm})(8.56 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(273 \text{ K})} = 0.57 \text{ mol}$$

See Exercises 5.35 through 5.40.



The reaction of zinc with hydrochloric acid to produce bubbles of hydrogen gas.

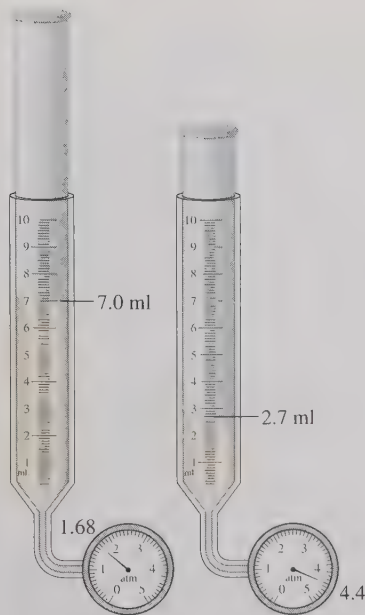
SAMPLE EXERCISE 5.7

Ideal Gas Law II

Suppose we have a sample of ammonia gas with a volume of 7.0 mL at a pressure of 1.68 atm. The gas is compressed to a volume of 2.7 mL at a constant temperature. Use the ideal gas law to calculate the final pressure.

SOLUTION

The basic assumption we make when using the ideal gas law to describe a change in state for a gas is that the equation applies equally well to both the initial and the final states. In dealing with a change in state, we always *place the variables that change on one side of the equals sign and the constants on the other*. In this case



As pressure increases, the volume decreases.

the pressure and volume change, and the temperature and the number of moles remain constant (as does R , by definition). Thus we write the ideal gas law as

$$PV = nRT$$

$\nearrow$ Change $\nwarrow$ Remain constant

Since n and T remain the same in this case, we can write $P_1V_1 = nRT$ and $P_2V_2 = nRT$. Combining these gives

$$P_1V_1 = nRT = P_2V_2 \quad \text{or} \quad P_1V_1 = P_2V_2$$

We are given $P_1 = 1.68$ atm, $V_1 = 7.0$ mL, and $V_2 = 2.7$ mL. Solving for P_2 thus gives

$$P_2 = \left(\frac{V_1}{V_2}\right)P_1 = \left(\frac{7.0 \text{ mL}}{2.7 \text{ mL}}\right)1.68 \text{ atm} = 4.4 \text{ atm}$$

CHECK:

Does this answer make sense? The volume decreased (at constant temperature), so the pressure should increase, as the result of the calculation indicates. Note that the calculated final pressure is 4.4 atm. Most gases do not behave ideally above 1 atm. Therefore, we might find that if we *measured* the pressure of this gas sample, the observed pressure would differ slightly from 4.4 atm.

See Exercise 5.41.

SAMPLE EXERCISE 5.8

Ideal Gas Law III

A sample of methane gas that has a volume of 3.8 L at 5°C is heated to 86°C at constant pressure. Calculate its new volume.

SOLUTION

To solve this problem, we take the ideal gas law and segregate the changing variables and the constants by placing them on opposite sides of the equation. In this case, volume and temperature change, and the number of moles and pressure (and, of course, R) remain constant. Thus $PV = nRT$ becomes

$$\frac{V}{T} = \frac{nR}{P}$$

which leads to

$$\frac{V_1}{T_1} = \frac{nR}{P} \quad \text{and} \quad \frac{V_2}{T_2} = \frac{nR}{P}$$

Combining these gives

$$\frac{V_1}{T_1} = \frac{nR}{P} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

We are given

$$\begin{array}{ll} T_1 = 5^\circ\text{C} + 273 = 278 \text{ K} & T_2 = 86^\circ\text{C} + 273 = 359 \text{ K} \\ V_1 = 3.8 \text{ L} & V_2 = ? \end{array}$$

Thus

$$V_2 = \frac{T_2 V_1}{T_1} = \frac{(359 \text{ K})(3.8 \text{ L})}{278 \text{ K}} = 4.9 \text{ L}$$

CHECK:

Is the answer sensible? In this case the temperature increased (at constant pressure), so the volume should increase. Thus the answer makes sense.

See Exercises 5.43 and 5.44.

The problem in Sample Exercise 5.8 could be described as a “Charles’s law problem,” whereas the problem in Sample Exercise 5.7 might be called a “Boyle’s law problem.” In both cases, however, we started with the ideal gas law. The real advantage of using the ideal gas law is that it applies to virtually any problem dealing with gases and is easy to remember.

SAMPLE EXERCISE 5.9

Ideal Gas Law IV

A sample of diborane gas (B_2H_6), a substance that bursts into flame when exposed to air, has a pressure of 345 torr at a temperature of -15°C and a volume of 3.48 L. If conditions are changed so that the temperature is 36°C and the pressure is 468 torr, what will be the volume of the sample?

SOLUTION

Since, for this sample, pressure, temperature, and volume all change while the number of moles remains constant, we use the ideal gas law in the form

$$\frac{PV}{T} = nR$$

which leads to

$$\frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2} \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Then

$$V_2 = \frac{T_2 P_1 V_1}{T_1 P_2}$$

We have

$$P_1 = 345 \text{ torr}$$

$$P_2 = 468 \text{ torr}$$

$$T_1 = -15^\circ\text{C} + 273 = 258 \text{ K}$$

$$T_2 = 36^\circ\text{C} + 273 = 309 \text{ K}$$

$$V_1 = 3.48 \text{ L}$$

$$V_2 = ?$$

Thus

$$V_2 = \frac{(309 \text{ K})(345 \text{ torr})(3.48 \text{ L})}{(258 \text{ K})(468 \text{ torr})} = 3.07 \text{ L}$$

See Exercises 5.45 and 5.46.

Always convert the temperature to the Kelvin scale when applying the ideal gas law.

Since the equation used in Sample Exercise 5.9 involves a *ratio* of pressures, it was unnecessary to convert pressures to units of atmospheres. The units of torrs cancel. (You will obtain the same answer by inserting $P_1 = \frac{345}{760}$ and $P_2 = \frac{468}{760}$ into the equation.) However, temperature *must always* be converted to the Kelvin scale; since this conversion involves *addition* of 273, the conversion factor does not cancel. Be careful.

One of the many other types of problems dealing with gases that can be solved using the ideal gas law is illustrated in Sample Exercise 5.10.

SAMPLE EXERCISE 5.10

Ideal Gas Law V

A sample containing 0.35 mol argon gas at a temperature of 13°C and a pressure of 568 torr is heated to 56°C and a pressure of 897 torr. Calculate the change in volume that occurs.

SOLUTION

We use the ideal gas law to find the volume for each set of conditions:

State 1	State 2
$n_1 = 0.35 \text{ mol}$	$n_2 = 0.35 \text{ mol}$
$P_1 = 568 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.747 \text{ atm}$	$P_2 = 897 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.18 \text{ atm}$
$T_1 = 13^\circ\text{C} + 273 = 286 \text{ K}$	$T_2 = 56^\circ\text{C} + 273 = 329 \text{ K}$

Solving the ideal gas law for volume gives

$$V_1 = \frac{n_1 RT_1}{P_1} = \frac{(0.35 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(286 \text{ K})}{(0.747 \text{ atm})} = 11 \text{ L}$$

and

$$V_2 = \frac{n_2 RT_2}{P_2} = \frac{(0.35 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(329 \text{ K})}{(1.18 \text{ atm})} = 8.0 \text{ L}$$

Thus, in going from state 1 to state 2, the volume changes from 11 L to 8.0 L. The change in volume, ΔV (Δ is the Greek capital letter delta), is then

$$\Delta V = V_2 - V_1 = 8.0 \text{ L} - 11 \text{ L} = -3 \text{ L}$$

The *change* in volume is negative because the volume decreases. Note that for this problem (unlike Sample Exercise 5.9) the pressures must be converted from torrs to atmospheres, as required by the atmosphere part of the units for R , since each volume was found separately and the conversion factor does not cancel.

See Exercise 5.47.



Argon glowing in a discharge tube.

5.4 Gas Stoichiometry

Suppose we have 1 mole of an ideal gas at 0°C (273.2 K) and 1 atm. From the ideal gas law, the volume of the gas is given by

$$V = \frac{nRT}{P} = \frac{(1.000 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273.2 \text{ K})}{1.000 \text{ atm}} = 22.42 \text{ L}$$

This volume of 22.42 liters is the **molar volume** of an ideal gas (at 0°C and 1 atm). The measured molar volumes of several gases are listed in Table 5.2. Note that the molar volumes of some of the gases are very close to the ideal value, while others deviate significantly. Later in this chapter we will discuss some of the reasons for the deviations.

The conditions 0°C and 1 atm, called **standard temperature and pressure** (abbreviated **STP**), are common reference conditions for the properties of gases. For example, the molar volume of an ideal gas is 22.42 liters at STP (see Fig. 5.11).

When 273.15 K is used in this calculation, the molar volume obtained in Sample Exercise 5.3 is the same value as 22.41 L.

STP: 0°C and 1 atm

SAMPLE EXERCISE 5.11

Gas Stoichiometry I

A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N₂ are present?

SOLUTION

We could solve this problem using the ideal gas equation, but we can take a shortcut by using the molar volume of an ideal gas at STP. Since 1 mole of an ideal gas at STP has a volume of 22.42 L, 1.75 L of N₂ at STP will contain less than 1 mole. We can find how many moles using the ratio of 1.75 L to 22.42 L:

$$1.75 \text{ L N}_2 \times \frac{1 \text{ mol N}_2}{22.42 \text{ L N}_2} = 7.81 \times 10^{-2} \text{ mol N}_2$$

See Exercises 5.49 and 5.50.

Many chemical reactions involve gases. By assuming ideal behavior for these gases, we can carry out stoichiometric calculations if the pressure, volume, and temperature of the gases are known.

TABLE 5.2
Molar Volumes for Various
Gases at 0°C and 1 atm

Gas	Molar Volume (L)
Oxygen (O ₂)	22.397
Nitrogen (N ₂)	22.402
Hydrogen (H ₂)	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide (CO ₂)	22.260
Ammonia (NH ₃)	22.079

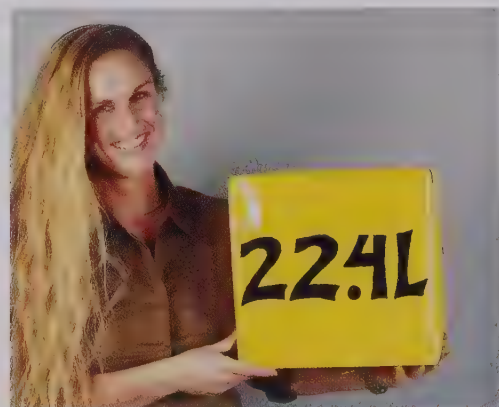


FIGURE 5.11
22.4 L of a gas would just fit into this box.

SAMPLE EXERCISE 5.12

Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate (CaCO₃). Calculate the volume of CO₂ at STP produced from the decomposition of 152 g CaCO₃ by the reaction



SOLUTION

We employ the same strategy we used in the stoichiometry problems earlier in this book. That is, we compute the number of moles of CaCO₃ consumed and the number of moles of CO₂ produced. The moles of CO₂ can then be converted to volume using the molar volume of an ideal gas.

Using the molar mass of CaCO₃ (100.09 g/mol), we can calculate the number of moles of CaCO₃:

$$152 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} = 1.52 \text{ mol CaCO}_3$$

Since each mole of CaCO₃ produces a mole of CO₂, 1.52 mol CO₂ will be formed. We can compute the volume of CO₂ at STP by using the molar volume:

$$1.52 \text{ mol CO}_2 \times \frac{22.42 \text{ L CO}_2}{1 \text{ mol CO}_2} = 34.1 \text{ L CO}_2$$

Thus the decomposition of 152 g CaCO₃ produces 34.1 L CO₂ at STP.

See Exercises 5.51 through 5.54.

Remember that the molar volume of an ideal gas is 22.42 L when measured at STP.

Note that in Sample Exercise 5.12 the final step involved calculation of the volume of gas from the number of moles. Since the conditions were specified as STP, we were able to use the molar volume of a gas at STP. If the conditions of a problem are different from STP, the ideal gas law must be used to compute the volume.

SAMPLE EXERCISE 5.13

Gas Stoichiometry III

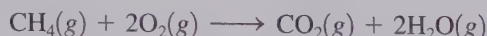
A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO₂ formed at a pressure of 2.50 atm and a temperature of 125°C.

SOLUTION

From the description of the reaction, the unbalanced equation is



which can be balanced to give



Next, we must find the limiting reactant, which requires calculating the numbers of moles of each reactant. We convert the given volumes of methane and oxygen to moles using the ideal gas law as follows:

$$n_{\text{CH}_4} = \frac{PV}{RT} = \frac{(1.65 \text{ atm})(2.80 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.189 \text{ mol}$$

$$n_{\text{O}_2} = \frac{PV}{RT} = \frac{(1.25 \text{ atm})(35.0 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(304 \text{ K})} = 1.75 \text{ mol}$$

In the balanced equation for the combustion reaction, 1 mol CH₄ requires 2 mol O₂. Thus the moles of O₂ required by 0.189 mol CH₄ can be calculated as follows:

$$0.189 \text{ mol CH}_4 \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = 0.378 \text{ mol O}_2$$

Since 1.75 mol O₂ is available, O₂ is in excess. The limiting reactant is CH₄. The number of moles of CH₄ available must be used to calculate the number of moles of CO₂ produced:

$$0.189 \text{ mol CH}_4 \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} = 0.189 \text{ mol CO}_2$$

Since the conditions stated are not STP, we must use the ideal gas law to calculate the volume:

$$V = \frac{nRT}{P}$$

In this case $n = 0.189 \text{ mol}$, $T = 125^\circ\text{C} + 273 = 398 \text{ K}$, $P = 2.50 \text{ atm}$, and $R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$. Thus

$$V = \frac{(0.189 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(398 \text{ K})}{2.50 \text{ atm}} = 2.47 \text{ L}$$

This represents the volume of CO₂ produced under these conditions.

See Exercises 5.55 and 5.56.

Molar Mass of a Gas

One very important use of the ideal gas law is in the calculation of the molar mass (molecular weight) of a gas from its measured density. To see the relationship between gas density and molar mass, consider that the number of moles of gas n can be expressed as

$$n = \frac{\text{grams of gas}}{\text{molar mass}} = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{\text{molar mass}}$$

Substitution into the ideal gas equation gives

$$P = \frac{nRT}{V} = \frac{(m/\text{molar mass})RT}{V} = \frac{m(RT)}{V(\text{molar mass})}$$

However, m/V is the gas density d in units of grams per liter. Thus

$$P = \frac{dRT}{\text{molar mass}}$$

or

$$\text{Molar mass} = \frac{dRT}{P} \quad (5.1)$$

Thus, if the density of a gas at a given temperature and pressure is known, its molar mass can be calculated.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

SAMPLE EXERCISE 5.14

Gas Density/Molar Mass

The density of a gas was measured at 1.50 atm and 27°C and found to be 1.95 g/L. Calculate the molar mass of the gas.

SOLUTION

Using Equation (5.1), we calculate the molar mass as follows:

$$\text{Molar mass} = \frac{dRT}{P} = \frac{\left(1.95 \frac{\text{g}}{\text{L}}\right) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) (300. \text{K})}{1.50 \text{ atm}} = 32.0 \text{ g/mol}$$

CHECK:

These are the units expected for molar mass.

See Exercises 5.59 through 5.62.

You could memorize the equation involving gas density and molar mass, but it is better simply to remember the total gas equation, the definition of density, and the relationship between number of moles and molar mass. You can then derive the appropriate equation when you need it. This approach ensures that you understand the concepts and means one less equation to memorize.

5.5 Dalton's Law of Partial Pressures

Among the experiments that led John Dalton to propose the atomic theory were his studies of mixtures of gases. In 1803 Dalton summarized his observations as follows: *For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.* This statement, known as **Dalton's law of partial pressures**, can be expressed as follows:

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots$$

where the subscripts refer to the individual gases (gas 1, gas 2, and so on). The symbols P_1 , P_2 , P_3 , and so on represent each **partial pressure**, that is, the pressure that a particular gas would exert if it were alone in the container.

Assuming that each gas behaves ideally, the partial pressure of each gas can be calculated from the ideal gas law:

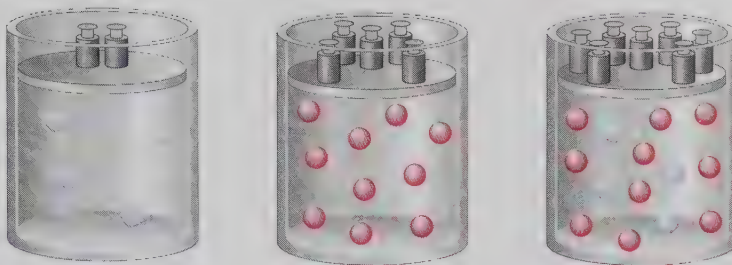
$$P_1 = \frac{n_1 RT}{V}, \quad P_2 = \frac{n_2 RT}{V}, \quad P_3 = \frac{n_3 RT}{V}, \quad \cdots$$

The total pressure of the mixture P_{TOTAL} can be represented as

$$\begin{aligned} P_{\text{TOTAL}} &= P_1 + P_2 + P_3 + \cdots = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \cdots \\ &= (n_1 + n_2 + n_3 + \cdots) \left(\frac{RT}{V} \right) \\ &= n_{\text{TOTAL}} \left(\frac{RT}{V} \right) \end{aligned}$$

FIGURE 5.12

The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas. The total pressure is the sum of the partial pressures and depends on the total moles of gas particles present, no matter what they are.



where n_{TOTAL} is the sum of the numbers of moles of the various gases. Thus, for a mixture of ideal gases, it is the *total number of moles of particles* that is important, not the identity or composition of the involved gas particles. This idea is illustrated in Fig. 5.12.

This important observation indicates some fundamental characteristics of an ideal gas. The fact that the pressure exerted by an ideal gas is not affected by the identity (composition) of the gas particles reveals two things about ideal gases: (1) the volume of the individual gas particle must not be important, and (2) the forces among the particles must not be important. If these factors were important, the pressure exerted by the gas would depend on the nature of the individual particles. These observations will strongly influence the model that we will eventually construct to explain ideal gas behavior.

SAMPLE EXERCISE 5.15

Dalton's Law I

Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent “the bends.” For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O₂ at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

SOLUTION

The first step is to calculate the number of moles of each gas using the ideal gas law in the form:

$$n = \frac{PV}{RT}$$

$$n_{\text{He}} = \frac{(1.0 \text{ atm})(46 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 1.9 \text{ mol}$$

$$n_{\text{O}_2} = \frac{(1.0 \text{ atm})(12 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 0.49 \text{ mol}$$

The tank containing the mixture has a volume of 5.0 L, and the temperature is 25°C. We can use these data and the ideal gas law to calculate the partial pressure of each gas:

$$P = \frac{nRT}{V}$$

$$P_{\text{He}} = \frac{(1.9 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{5.0 \text{ L}} = 9.3 \text{ atm}$$

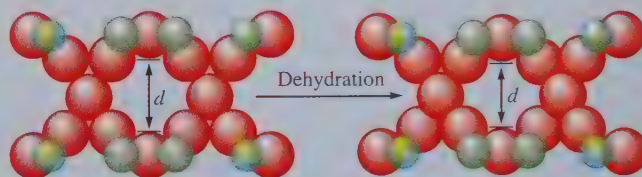
$$P_{\text{O}_2} = \frac{(0.49 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{5.0 \text{ L}} = 2.4 \text{ atm}$$

Separating Gases

Assume you work for an oil company that owns a huge natural gas reservoir containing a mixture of methane and nitrogen gases. In fact, the gas mixture contains so much nitrogen that it is unusable as a fuel. Your job is to separate the nitrogen (N_2) from the methane (CH_4). How might you accomplish this task? You clearly need some sort of “molecular filter” that will stop the slightly larger methane molecules (size ≈ 430 pm) and allow the nitrogen molecules (size ≈ 410 pm) to pass through. To accomplish the separation of molecules so similar in size will require a very precise “filter.”

The good news is that such a filter exists. Recent work by Steven Kuznick and Valerie Bell at Engelhard Corporation in New Jersey and Michael Tsapatsis at the University of Massachusetts has produced a “molecular sieve” in which the pore (passage) sizes can be adjusted precisely enough to separate N_2 molecules from CH_4 molecules. The material involved is a special hydrated titanosilicate (contains H_2O , Ti, Si, O, and Sr) compound patented by Engelhard known

as ETS-4 (Engelhard TitanoSilicate-4). When sodium ions are substituted for the strontium ions in ETS-4 and the new material is carefully dehydrated, a uniform and controllable pore-size reduction occurs (see figure). The researchers have shown that the material can be used to separate N_2 (≈ 410 pm) from O_2 (≈ 390 pm). They have also shown that it is possible to reduce the nitrogen content of natural gas from 18% to less than 5% with a 90% recovery of methane.



Molecular sieve framework of titanium (blue), silicon (green), and oxygen (red) atoms contracts on heating—at room temperature (left), $d = 4.27$ Å; at 250 °C (right), $d = 3.94$ Å.

The total pressure is the sum of the partial pressures:

$$P_{\text{TOTAL}} = P_{\text{He}} + P_{\text{O}_2} = 9.3 \text{ atm} + 2.4 \text{ atm} = 11.7 \text{ atm}$$

See Exercises 5.63 and 5.64.

At this point we need to define the **mole fraction**: *the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.* The Greek lowercase letter chi (χ) is used to symbolize the mole fraction. For example, for a given component in a mixture, the mole fraction χ_1 is

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

From the ideal gas equation we know that the number of moles of a gas is directly proportional to the pressure of the gas, since

$$n = P \left(\frac{V}{RT} \right)$$

That is, for each component in the mixture,

$$n_1 = P_1 \left(\frac{V}{RT} \right), \quad n_2 = P_2 \left(\frac{V}{RT} \right), \quad \dots$$

Therefore, we can represent the mole fraction in terms of pressures:

$$\begin{aligned}
 \chi_1 &= \frac{n_1}{n_{\text{TOTAL}}} = \frac{\overbrace{P_1(V/RT)}^{n_1}}{\underbrace{P_1(V/RT)}_{n_1} + \underbrace{P_2(V/RT)}_{n_2} + \underbrace{P_3(V/RT)}_{n_3} + \cdots} \\
 &= \frac{(V/RT)P_1}{(V/RT)(P_1 + P_2 + P_3 + \cdots)} \\
 &= \frac{P_1}{P_1 + P_2 + P_3 + \cdots} = \frac{P_1}{P_{\text{TOTAL}}}
 \end{aligned}$$

In fact, the mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure:

$$\chi_2 = \frac{n_2}{n_{\text{TOTAL}}} = \frac{P_2}{P_{\text{TOTAL}}}$$

SAMPLE EXERCISE 5.16

Dalton's Law II

The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

SOLUTION

The mole fraction of O_2 can be calculated from the equation

$$\chi_{\text{O}_2} = \frac{P_{\text{O}_2}}{P_{\text{TOTAL}}} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

Note that mole fraction has no units.

See Exercise 5.67.

The expression for the mole fraction,

$$\chi_1 = \frac{P_1}{P_{\text{TOTAL}}}$$

can be rearranged to give

$$P_1 = \chi_1 \times P_{\text{TOTAL}}$$

That is, *the partial pressure of a particular component of a gaseous mixture is the mole fraction of that component times the total pressure.*

SAMPLE EXERCISE 5.17

Dalton's Law III

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. torr.

SOLUTION

The partial pressure of N_2 can be calculated as follows:

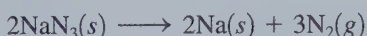
$$P_{\text{N}_2} = \chi_{\text{N}_2} \times P_{\text{TOTAL}} = 0.7808 \times 760. \text{ torr} = 593 \text{ torr}$$

See Exercise 5.68.

CHEMICAL IMPACT

The Chemistry of Air Bags

Most experts agree that air bags represent a very important advance in automobile safety. These bags, which are stored in the auto's steering wheel or dash, are designed to inflate rapidly (within about 40 ms) in the event of a crash, cushioning the front-seat occupants against impact. The bags then deflate immediately to allow vision and movement after the crash. Air bags are activated when a severe deceleration (an impact) causes a steel ball to compress a spring and electrically ignite a detonator cap, which, in turn, causes sodium azide (NaN_3) to decompose explosively, forming sodium and nitrogen gas:



This system works very well and requires a relatively small amount of sodium azide (100 g yields 56 L $\text{N}_2(g)$ at 25°C and 1.0 atm).

When a vehicle containing air bags reaches the end of its useful life, the sodium azide present in the activators must be given proper disposal. Sodium azide, besides being explosive, has a toxicity roughly equal to that of sodium

cyanide. It also forms hydrazoic acid (HN_3), a toxic and explosive liquid, when treated with acid.

The air bag represents an application of chemistry that has already saved thousands of lives.



Inflated air bags.

Vapor pressure will be discussed in detail in Chapter 10. A table of water vapor pressure values is given in Section 10.8.

A mixture of gases results whenever a gas is collected by displacement of water. For example, Fig. 5.13 shows the collection of oxygen gas produced by the decomposition of solid potassium chlorate. In this situation, the gas in the bottle is a mixture of water vapor and the oxygen being collected. Water vapor is present because molecules of water escape from the surface of the liquid and collect in the space above the liquid. Molecules of water also return to the liquid. When the rate of escape equals the rate of return, the number of water molecules in the vapor state remains

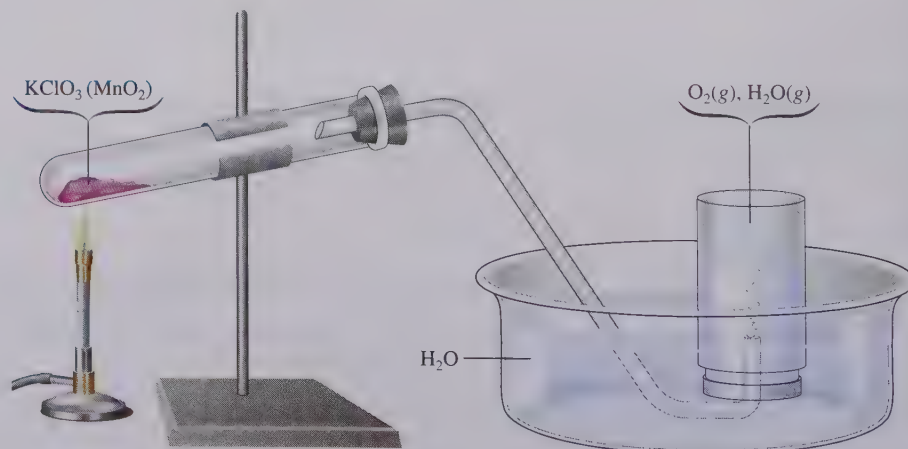


FIGURE 5.13

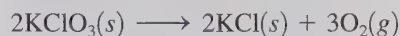
The production of oxygen by thermal decomposition of KClO_3 . The MnO_2 is mixed with the KClO_3 to make the reaction faster.

constant, and thus the pressure of water vapor remains constant. This pressure, which depends on temperature, is called the *vapor pressure of water*.

SAMPLE EXERCISE 5.18

Gas Collection over Water

A sample of solid potassium chlorate (KClO_3) was heated in a test tube (see Fig. 5.13) and decomposed by the following reaction:



The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of KClO_3 in the sample that was decomposed.

SOLUTION

First we find the partial pressure of O_2 from Dalton's law of partial pressures:

$$P_{\text{TOTAL}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}} = P_{\text{O}_2} + 21 \text{ torr} = 754 \text{ torr}$$

Thus

$$P_{\text{O}_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr}$$

Now we use the ideal gas law to find the number of moles of O_2 :

$$n_{\text{O}_2} = \frac{P_{\text{O}_2}V}{RT}$$

In this case,

$$P_{\text{O}_2} = 733 \text{ torr} = \frac{733 \text{ torr}}{760 \text{ torr/atm}} = 0.964 \text{ atm}$$

$$V = 0.650 \text{ L}$$

$$T = 22^\circ\text{C} + 273 = 295 \text{ K}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

Thus

$$n_{\text{O}_2} = \frac{(0.964 \text{ atm})(0.650 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})} = 2.59 \times 10^{-2} \text{ mol}$$

Next we will calculate the moles of KClO_3 needed to produce this quantity of O_2 . From the balanced equation for the decomposition of KClO_3 , we have a mole ratio of 2 mol KClO_3 /3 mol O_2 . The moles of KClO_3 can be calculated as follows:

$$2.59 \times 10^{-2} \text{ mol O}_2 \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} = 1.73 \times 10^{-2} \text{ mol KClO}_3$$

Using the molar mass of KClO_3 (122.6 g/mol), we calculate the grams of KClO_3 :

$$1.73 \times 10^{-2} \text{ mol KClO}_3 \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 2.12 \text{ g KClO}_3$$

Thus the original sample contained 2.12 g KClO_3 .

See Exercises 5.69 through 5.71.

5.6 The Kinetic Molecular Theory of Gases

We have so far considered the behavior of gases from an experimental point of view. Based on observations from different types of experiments, we know that at pressures of less than 1 atm most gases closely approach the behavior described by the ideal gas law. Now we want to construct a model to explain this behavior.

Before we do this, let's briefly review the scientific method. Recall that a law is a way of generalizing behavior that has been observed in many experiments. Laws are very useful, since they allow us to predict the behavior of similar systems. For example, if a chemist prepares a new gaseous compound, a measurement of the gas density at known pressure and temperature can provide a reliable value for the compound's molar mass.

However, although laws summarize observed behavior, they do not tell us *why* nature behaves in the observed fashion. This is the central question for scientists. To try to answer this question, we construct theories (build models). The models in chemistry consist of speculations about what the individual atoms or molecules (microscopic particles) might be doing to cause the observed behavior of the macroscopic systems (collections of very large numbers of atoms and molecules).

A model is considered successful if it explains the observed behavior in question and predicts correctly the results of future experiments. It is important to understand that a model can never be proved absolutely true. In fact, *any model is an approximation* by its very nature and is bound to fail at some point. Models range from the simple to the extraordinarily complex. We use simple models to predict approximate behavior and more complicated models to account very precisely for observed quantitative behavior. In this text we will stress simple models that provide an approximate picture of what might be happening and that fit the most important experimental results.

An example of this type of model is the **kinetic molecular theory (KMT)**, a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of the individual gas particles (atoms or molecules). The postulates of the kinetic molecular theory as they relate to the particles of an ideal gas can be stated as follows:

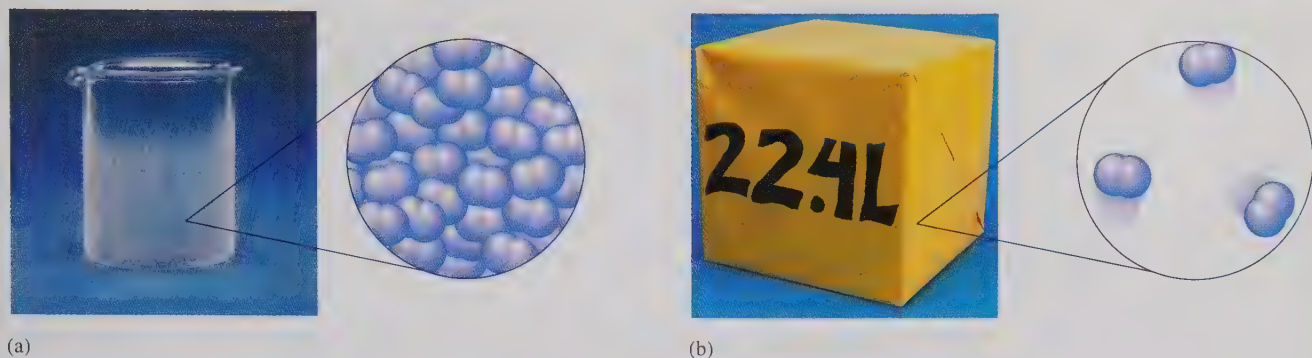
1. The particles are so small compared with the distances between them that *the volume of the individual particles can be assumed to be negligible (zero)*. See Fig. 5.14.
2. *The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.*
3. *The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.*
4. *The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.*

Of course, the molecules in a real gas have finite volumes and do exert forces on each other. Thus *real gases* do not conform to these assumptions. However, we will see that these postulates do indeed explain *ideal gas* behavior.

The true test of a model is how well its predictions fit the experimental observations. The postulates of the kinetic molecular model picture an ideal gas as con-



Visualization: Visualizing Molecular Motion (Single Molecule and Many Molecules)

**FIGURE 5.14**

(a) One mole of $\text{N}_2(\ell)$ has a volume of approximately 35 mL and a density of 0.81 g/mL. (b) One mole of $\text{N}_2(g)$ has a volume of 22.4 L (STP) and a density of 1.2×10^{-3} g/mL. Thus the ratio of the volumes of gaseous N_2 and liquid N_2 is $22.4/0.035 = 640$ and the spacing of the molecules is 9 times farther apart in $\text{N}_2(g)$.

sisting of particles having no volume and no attractions for each other, and the model assumes that the gas produces pressure on its container by collisions with the walls.

Let's consider how this model accounts for the properties of gases as summarized by the ideal gas law: $PV = nRT$.

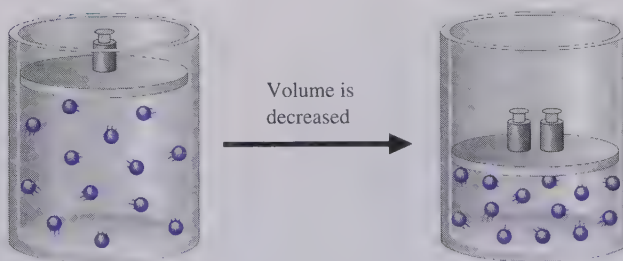
Pressure and Volume (Boyle's Law)

We have seen that for a given sample of gas at a given temperature (n and T are constant) that if the volume of a gas is decreased, the pressure increases:

$$P = (nRT) \frac{1}{V}$$

$\uparrow$
 Constant

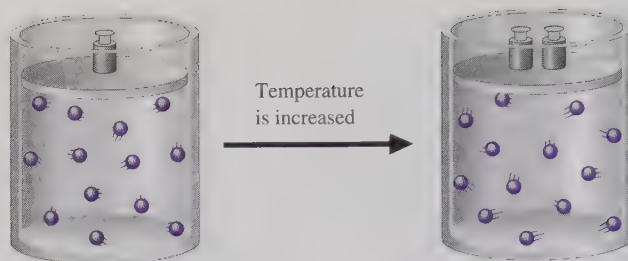
This makes sense based on the kinetic molecular theory, since a decrease in volume means that the gas particles will hit the wall more often, thus increasing pressure, as illustrated in Fig. 5.15.

**FIGURE 5.15**

The effects of decreasing the volume of a sample of gas at constant temperature.



Visualization: Microscopic Illustration of Boyle's Law

**FIGURE 5.16**

The effects of increasing the temperature of a sample of gas at constant volume.

Pressure and Temperature

From the ideal gas law we can predict that for a given sample of an ideal gas at a constant volume, the pressure will be directly proportional to the temperature:

$$P = \left(\frac{nR}{V} \right) T$$

$\uparrow$
 Constant

The KMT accounts for this behavior because when the temperature of a gas increases, the speeds of its particles increase, the particles hitting the wall with greater force and greater frequency. Since the volume remains the same, this would result in increased gas pressure, as illustrated in Fig. 5.16.

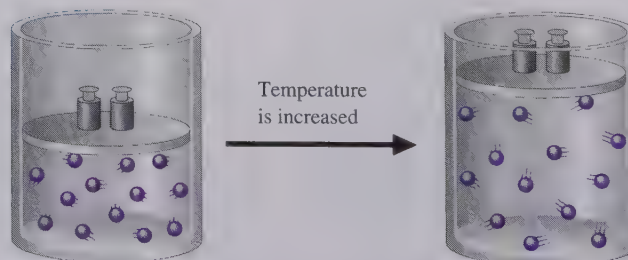
Volume and Temperature (Charles's Law)

The ideal gas law indicates that for a given sample of gas at a constant pressure, the volume of the gas is directly proportional to the temperature in kelvins:

$$V = \left(\frac{nR}{P} \right) T$$

$\uparrow$
 Constant

This can be visualized from the KMT, as shown in Fig. 5.17. When the gas is heated to a higher temperature, the speeds of its molecules increase and thus they hit the

**FIGURE 5.17**

The effects of increasing the temperature of a sample of gas at constant pressure.



Visualization: Microscopic Illustration of Charles's Law

walls more often and with more force. The only way to keep the pressure constant in this situation is to increase the volume of the container. This compensates for the increased particle speeds.

Volume and Number of Moles (Avogadro's Law)

The ideal gas law predicts that the volume of a gas at a constant temperature and pressure depends directly on the number of gas particles present:

$$V = \left(\frac{RT}{P} \right) n$$

↑
Constant

This makes sense in terms of the KMT, because an increase in the number of gas particles at the same temperature would cause the pressure to increase if the volume were held constant (see Fig. 5.18). The only way to return the pressure to its original value is to increase the volume.

It is important to recognize that the volume of a gas (at constant P and T) depends only on the *number* of gas particles present. The individual volumes of the particles are not a factor because the particle volumes are so small compared with the distances between the particles (for a gas behaving ideally).

Mixture of Gases (Dalton's Law)

The observation that the total pressure exerted by a mixture of gases is the sum of the pressures of the individual gases is expected because the KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant. Thus the identities of the gas particles do not matter.

Deriving the Ideal Gas Law

We have shown qualitatively that the assumptions of the KMT successfully account for the observed behavior of an ideal gas. We can go further. By applying the principles of physics to the assumptions of the KMT, we can in effect derive the ideal gas law.

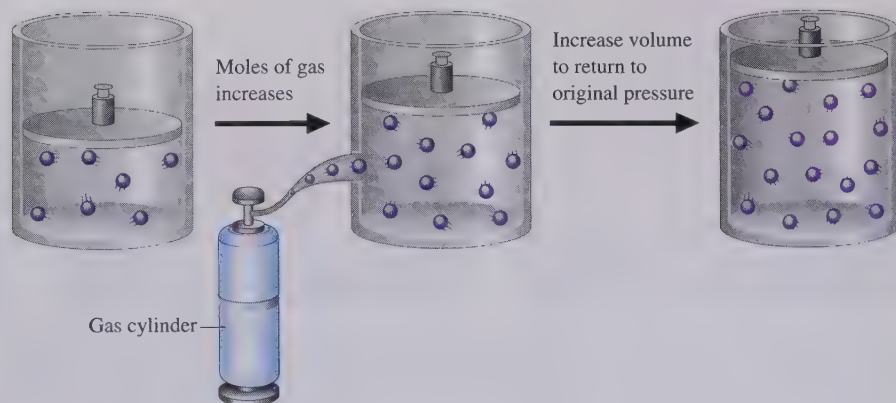


FIGURE 5.18

The effects of increasing the number of moles of gas particles at constant temperature and pressure.

As shown in detail in Appendix 2, we can apply the definitions of velocity, momentum, force, and pressure to the collection of particles in an ideal gas and derive the following expression for pressure:

$$P = \frac{2}{3} \left[\frac{nN_A(\frac{1}{2}m\bar{u}^2)}{V} \right]$$

where P is the pressure of the gas, n is the number of moles of gas, N_A is Avogadro's number, m is the mass of each particle, $\bar{u}^2$ is the average of the square of the velocities of the particles, and V is the volume of the container.

The quantity $\frac{1}{2}m\bar{u}^2$ represents the average kinetic energy of a gas particle. If the average kinetic energy of an individual particle is multiplied by N_A , the number of particles in a mole, we get the average kinetic energy for a mole of gas particles:

$$(\text{KE})_{\text{avg}} = N_A(\frac{1}{2}m\bar{u}^2)$$

Using this definition, we can rewrite the expression for pressure as

$$P = \frac{2}{3} \left[\frac{n(\text{KE})_{\text{avg}}}{V} \right] \quad \text{or} \quad \frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}}$$

The fourth postulate of the kinetic molecular theory is that the average kinetic energy of the particles in the gas sample is directly proportional to the temperature in Kelvins. Thus, since $(\text{KE})_{\text{avg}} \propto T$, we can write

$$\frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}} \propto T \quad \text{or} \quad \frac{PV}{n} \propto T$$

Note that this expression has been *derived* from the assumptions of the kinetic molecular theory. How does it compare to the ideal gas law—the equation obtained from experiment? Compare the ideal gas law,

$$\frac{PV}{n} = RT \quad \text{From experiment}$$

Kinetic energy (KE) given by the equation $\text{KE} = \frac{1}{2}mu^2$ is the energy due to the motion of a particle. We will discuss this further in Section 6.1.



Visualization: Liquid Nitrogen and Balloons



(a) A balloon filled with air at room temperature. (b) The balloon is dipped into liquid nitrogen at 77 K. (c) The balloon collapses as the molecules inside slow down due to the decreased temperature. Slower molecules produce a lower pressure.

with the result from the kinetic molecular theory,

$$\frac{PV}{n} \propto T \quad \text{From theory}$$

These expressions have exactly the same form if R , the universal gas constant, is considered the proportionality constant in the second case.

The agreement between the ideal gas law and the predictions of the kinetic molecular theory gives us confidence in the validity of the model. The characteristics we have assumed for ideal gas particles must agree, at least under certain conditions, with their actual behavior.

The Meaning of Temperature

We have seen from the kinetic molecular theory that the Kelvin temperature indicates the average kinetic energy of the gas particles. The exact relationship between temperature and average kinetic energy can be obtained by combining the equations:

$$\frac{PV}{n} = RT = \frac{2}{3}(\text{KE})_{\text{avg}}$$

which yields the expression

$$(\text{KE})_{\text{avg}} = \frac{3}{2}RT$$

This is a very important relationship. It summarizes the meaning of the Kelvin temperature of a gas: The Kelvin temperature is an index of the random motions of the particles of a gas, with higher temperature meaning greater motion. (As we will see in Chapter 10, temperature is an index of the random motions in solids and liquids as well as in gases.)

Root Mean Square Velocity

In the equation from the kinetic molecular theory, the average velocity of the gas particles is a special kind of average. The symbol $\overline{u^2}$ means the average of the *squares* of the particle velocities. The square root of $\overline{u^2}$ is called the **root mean square velocity** and is symbolized by u_{rms} :

$$u_{\text{rms}} = \sqrt{\overline{u^2}}$$

We can obtain an expression for u_{rms} from the equations

$$(\text{KE})_{\text{avg}} = N_A \left(\frac{1}{2} m \overline{u^2} \right) \quad \text{and} \quad (\text{KE})_{\text{avg}} = \frac{3}{2} RT$$

Combination of these equations gives

$$N_A \left(\frac{1}{2} m \overline{u^2} \right) = \frac{3}{2} RT \quad \text{or} \quad \overline{u^2} = \frac{3RT}{N_A m}$$

Taking the square root of both sides of the last equation produces

$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{N_A m}}$$

In this expression m represents the mass in kilograms of a single gas particle. When N_A , the number of particles in a mole, is multiplied by m , the product is the mass of a *mole* of gas particles in *kilograms*. We will call this quantity M . Substituting M for $N_A m$ in the equation for u_{rms} , we obtain

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Before we can use this equation, we need to consider the units for R . So far we have used $0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$ as the value of R . But to obtain the desired units (meters per second) for u_{rms} , R must be expressed in different units. As we will see in more detail in Chapter 6, the energy unit most often used in the SI system is the joule (J). A **joule** is defined as a kilogram meter squared per second squared ($\text{kg} \cdot \text{m}^2/\text{s}^2$). When R is converted to include the unit of joules, it has the value $8.3145 \text{ J}/\text{K} \cdot \text{mol}$. When R in these units is used in the expression $\sqrt{3RT/M}$, u_{rms} is obtained in the units of meters per second as desired.

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

SAMPLE EXERCISE 5.19

Root Mean Square Velocity

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C .

SOLUTION

The formula for root mean square velocity is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

In this case $T = 25^\circ\text{C} + 273 = 298 \text{ K}$, $R = 8.3145 \text{ J}/\text{K} \cdot \text{mol}$, and M is the mass of a mole of helium in kilograms:

$$M = 4.00 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 4.00 \times 10^{-3} \text{ kg/mol}$$

Thus

$$u_{\text{rms}} = \sqrt{\frac{3 \left(8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) (298 \text{ K})}{4.00 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}} = \sqrt{1.86 \times 10^6 \frac{\text{J}}{\text{kg}}}$$

Since the units of J are $\text{kg} \cdot \text{m}^2/\text{s}^2$, this expression becomes

$$\sqrt{1.86 \times 10^6 \frac{\text{kg} \cdot \text{m}^2}{\text{kg} \cdot \text{s}^2}} = 1.36 \times 10^3 \text{ m/s}$$

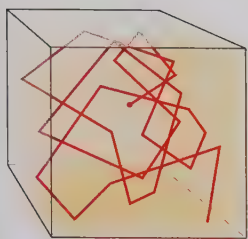
Note that the resulting units (m/s) are appropriate for velocity.

See Exercises 5.75 and 5.76.

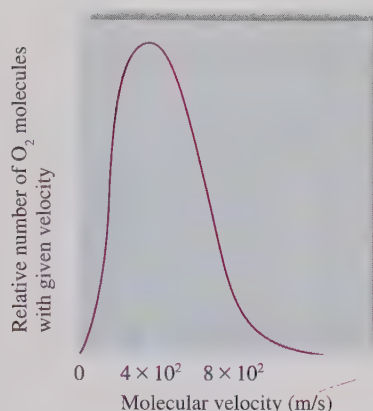


Visualization: The Kinetic Molecular Theory and Heat Transfer

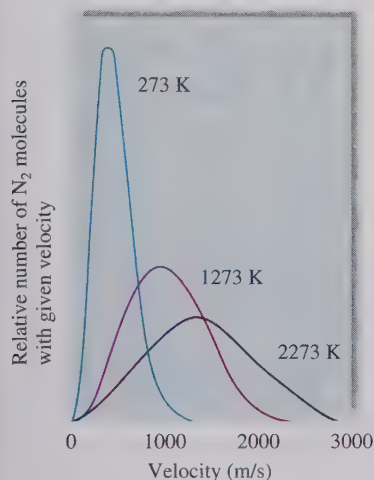
So far we have said nothing about the range of velocities actually found in a gas sample. In a real gas there are large numbers of collisions between particles. For example, as we will see in the next section, when an odorous gas such as ammonia is released in a room, it takes some time for the odor to permeate the air. This

**FIGURE 5.19**

Path of one particle in a gas. Any given particle will continuously change its course as a result of collisions with other particles, as well as with the walls of the container.

**FIGURE 5.20**

A plot of the relative number of O_2 molecules that have a given velocity at STP.

**FIGURE 5.21**

A plot of the relative number of N_2 molecules that have a given velocity at three temperatures. Note that as the temperature increases, both the average velocity and the spread of velocities increase.

delay results from collisions between the NH_3 molecules and the O_2 and N_2 molecules in the air, which greatly slow the mixing process.

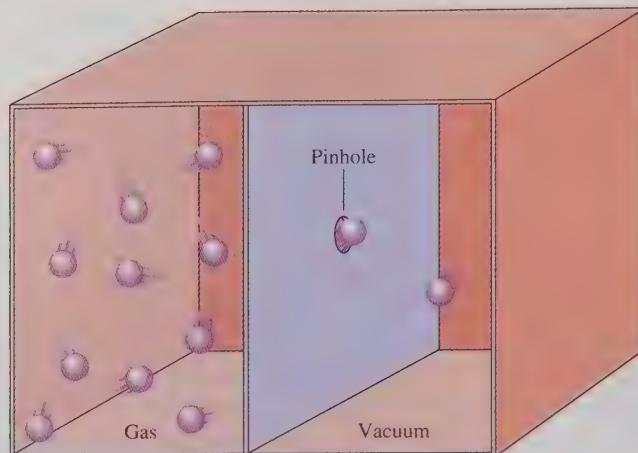
If the path of a particular gas particle could be monitored, it would look very erratic, something like that shown in Fig. 5.19. The average distance a particle travels between collisions in a particular gas sample is called the *mean free path*. It is typically a very small distance (1×10^{-7} m for O_2 at STP). One effect of the many collisions among gas particles is to produce a large range of velocities as the particles collide and exchange kinetic energy. Although u_{rms} for oxygen gas at STP is approximately 500 meters per second, the majority of O_2 molecules do not have this velocity. The actual distribution of molecular velocities for oxygen gas at STP is shown in Fig. 5.20. This figure shows the relative number of gas molecules having each particular velocity.

We are also interested in the effect of *temperature* on the velocity distribution in a gas. Figure 5.21 shows the velocity distribution for nitrogen gas at three temperatures. Note that as the temperature is increased, the curve peak moves toward higher values and the range of velocities becomes much larger. The peak of the curve reflects the most probable velocity (the velocity found most often as we sample the movement of the various particles in the gas). Because the kinetic energy increases with temperature, it makes sense that the peak of the curve should move to higher values as the temperature of the gas is increased.

5.7 Effusion and Diffusion

We have seen that the postulates of the kinetic molecular theory, when combined with the appropriate physical principles, produce an equation that successfully fits the experimentally observed behavior of gases as they approach ideal behavior. Two phenomena involving gases provide further tests of this model.

Diffusion is the term used to describe the mixing of gases. When a small amount of pungent-smelling ammonia is released at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the ammonia to mix with the air. The rate of diffusion is the rate of the mixing of gases.

**FIGURE 5.22**

The effusion of a gas into an evacuated chamber. The rate of effusion (the rate at which the gas is transferred across the barrier through the pin hole) is inversely proportional to the square root of the mass of the gas molecules.

Effusion is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber, as shown in Fig. 5.22. The rate of effusion measures the speed at which the gas is transferred into the chamber.

Effusion

Thomas Graham (1805–1869), a Scottish chemist, found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. Stated in another way, the relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles:

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

In Graham's law the units for molar mass can be g/mol or kg/mol, since the units cancel in the ratio $\sqrt{M_2}/\sqrt{M_1}$.

where M_1 and M_2 represent the molar masses of the gases. This equation is called **Graham's law of effusion**.

SAMPLE EXERCISE 5.20

Effusion Rates

Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors (see Fig. 5.23).

SOLUTION

First we need to compute the molar masses: Molar mass of $\text{H}_2 = 2.016 \text{ g/mol}$, and molar mass of $\text{UF}_6 = 352.02 \text{ g/mol}$. Using Graham's law,

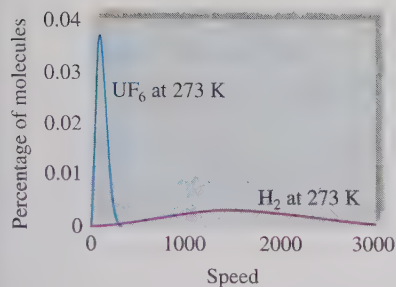
$$\frac{\text{Rate of effusion for } \text{H}_2}{\text{Rate of effusion for } \text{UF}_6} = \frac{\sqrt{M_{\text{UF}_6}}}{\sqrt{M_{\text{H}_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

The effusion rate of the very light H_2 molecules is about 13 times that of the massive UF_6 molecules.



Visualization: The Effusion of a Gas

See Exercises 5.81 through 5.84.

**FIGURE 5.23**

Relative molecular speed distribution of H_2 and UF_6 .

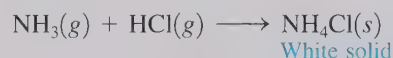
Does the kinetic molecular model for gases correctly predict the relative effusion rates of gases summarized by Graham's law? To answer this question, we must recognize that the effusion rate for a gas depends directly on the average velocity of its particles. The faster the gas particles are moving, the more likely they are to pass through the effusion orifice. This reasoning leads to the following *prediction* for two gases at the same pressure and temperature (T):

$$\frac{\text{Effusion rate for gas 1}}{\text{Effusion rate for gas 2}} = \frac{u_{\text{rms}} \text{ for gas 1}}{u_{\text{rms}} \text{ for gas 2}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

This equation is identical to Graham's law. Thus the kinetic molecular model does fit the experimental results for the effusion of gases.

Diffusion

Diffusion is frequently illustrated by the lecture demonstration represented in Fig. 5.24, in which two cotton plugs soaked in ammonia and hydrochloric acid are simultaneously placed at the ends of a long tube. A white ring of ammonium chloride (NH_4Cl) forms where the NH_3 and HCl molecules meet several minutes later:

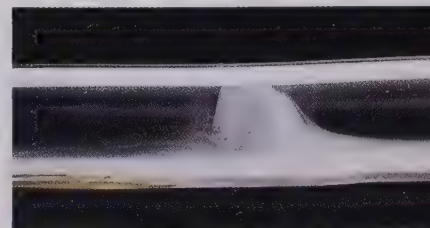
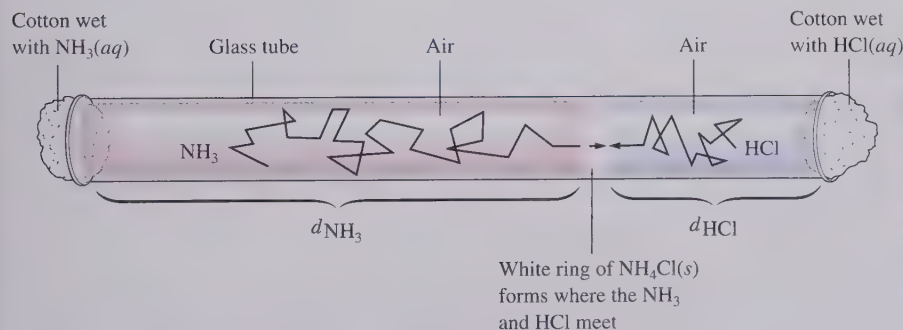


As a first approximation we might expect that the distances traveled by the two gases are related to the relative velocities of the gas molecules:

$$\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{\text{rms}} \text{ for NH}_3}{u_{\text{rms}} \text{ for HCl}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} = 1.5$$

However, careful experiments produce an observed ratio of less than 1.5, indicating that a quantitative analysis of diffusion requires a more complex analysis.

Visualization: Diffusion of Gases

**FIGURE 5.24**

(above right) When $\text{HCl}(g)$ and $\text{NH}_3(g)$ meet in the tube, a white ring of $\text{NH}_4\text{Cl}(s)$ forms. (above left) A demonstration of the relative diffusion rates of NH_3 and HCl molecules through air. Two cotton plugs, one dipped in $\text{HCl}(aq)$ and one dipped in $\text{NH}_3(aq)$, are simultaneously inserted into the ends of the tube. Gaseous NH_3 and HCl vaporizing from the cotton plugs diffuse toward each other and, where they meet, react to form $\text{NH}_4\text{Cl}(s)$.

The diffusion of the gases through the tube is surprisingly slow in light of the fact that the velocities of HCl and NH₃ molecules at 25°C are about 450 and 660 meters per second, respectively. Why does it take several minutes for the NH₃ and HCl molecules to meet? The answer is that the tube contains air and thus the NH₃ and HCl molecules undergo many collisions with O₂ and N₂ molecules as they travel through the tube. Because so many collisions occur when gases mix, diffusion is quite complicated to describe theoretically.

5.8 Real Gases

An ideal gas is a hypothetical concept. No gas *exactly* follows the ideal gas law, although many gases come very close at low pressures and/or high temperatures. Thus ideal gas behavior can best be thought of as the behavior *approached by real gases* under certain conditions.

We have seen that a very simple model, the kinetic molecular theory, by making some rather drastic assumptions (no interparticle interactions and zero volume for the gas particles), successfully explains ideal behavior. However, it is important that we examine real gas behavior to see how it differs from that predicted by the ideal gas law and to determine what modifications are needed in the kinetic molecular theory to explain the observed behavior. Since a model is an approximation and will inevitably fail, we must be ready to learn from such failures. In fact, we often learn more about nature from the failures of our models than from their successes.

We will examine the experimentally observed behavior of real gases by measuring the pressure, volume, temperature, and number of moles for a gas and noting how the quantity PV/nRT depends on pressure. Plots of PV/nRT versus P are shown for several gases in Fig. 5.25. For an ideal gas, PV/nRT equals 1 under all conditions, but notice that for real gases, PV/nRT approaches 1 only at very low pressures (typically below 1 atm). To illustrate the effect of temperature, PV/nRT is plotted versus P for nitrogen gas at several temperatures in Fig. 5.26. Note that the behavior of the gas appears to become more nearly ideal as the temperature is increased. The most important conclusion to be drawn from these figures is that a real gas typically exhibits behavior that is closest to ideal behavior at *low pressures* and *high temperatures*.

How can we modify the assumptions of the kinetic molecular theory to fit the behavior of real gases? An equation for real gases was developed in 1873 by Johannes van der Waals (1837–1923), a physics professor at the University of Amsterdam who in 1910 received a Nobel Prize for his work. To follow his analysis, we start with the ideal gas law,

$$P = \frac{nRT}{V}$$

Remember that this equation describes the behavior of a hypothetical gas consisting of volumeless entities that do not interact with each other. In contrast, a real gas consists of atoms or molecules that have finite volumes. Therefore, the volume available to a given particle in a real gas is less than the volume of the container because the gas particles themselves take up some of the space. To account for this discrepancy, van der Waals represented the actual volume as the volume of the con-

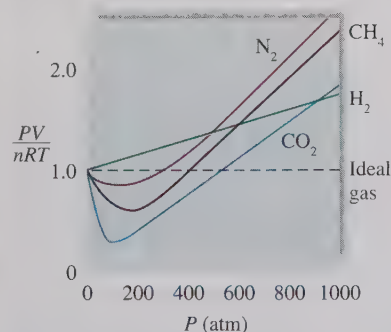


FIGURE 5.25

Plots of PV/nRT versus P for several gases (200 K). Note the significant deviations from ideal behavior ($PV/nRT = 1$). The behavior is close to ideal only at low pressures (less than 1 atm).

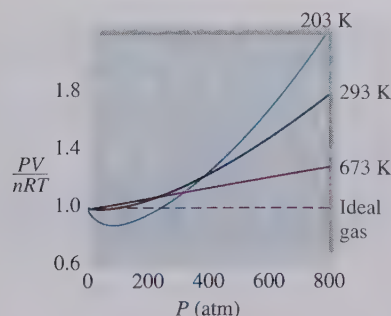


FIGURE 5.26

Plots of PV/nRT versus P for nitrogen gas at three temperatures. Note that although nonideal behavior is evident in each case, the deviations are smaller at the higher temperatures.

P' is corrected for the finite volume of the particles. The attractive forces have not yet been taken into account.

tainer V minus a correction factor for the volume of the molecules nb , where n is the number of moles of gas and b is an empirical constant (one determined by fitting the equation to the experimental results). Thus the volume *actually available* to a given gas molecule is given by the difference $V - nb$.

This modification of the ideal gas equation leads to the equation

$$P' = \frac{nRT}{V - nb}$$

The volume of the gas particles has now been taken into account.

The next step is to allow for the attractions that occur among the particles in a real gas. The effect of these attractions is to make the observed pressure P_{obs} smaller than it would be if the gas particles did not interact:

$$P_{\text{obs}} = (P' - \text{correction factor}) = \left(\frac{nRT}{V - nb} - \text{correction factor} \right)$$

The attractive forces among molecules will be discussed in Chapter 10.

This effect can be understood using the following model. When gas particles come close together, attractive forces occur, which cause the particles to hit the wall very slightly less often than they would in the absence of these interactions (see Fig. 5.27).

The size of the correction factor depends on the concentration of gas molecules defined in terms of moles of gas particles per liter (n/V). The higher the concentration, the more likely a pair of gas particles will be close enough to attract each other. For large numbers of particles, the number of interacting *pairs* of particles depends on the square of the number of particles and thus on the square of the concentration, or $(n/V)^2$. This can be justified as follows: In a gas sample containing N particles, there are $N - 1$ partners available for each particle, as shown in Fig. 5.28. Since the $1 \cdots 2$ pair is the same as the $2 \cdots 1$ pair, this analysis counts each pair twice. Thus, for N particles, there are $N(N - 1)/2$ pairs. If N is a very large number, $N - 1$ approximately equals N , giving $N^2/2$ possible pairs. Thus the pressure, corrected for the attractions of the particles, has the form

$$P_{\text{obs}} = P' - a \left(\frac{n}{V} \right)^2$$

where a is a proportionality constant (which includes the factor of $\frac{1}{2}$ from $N^2/2$). The value of a for a given real gas can be determined from observing the actual

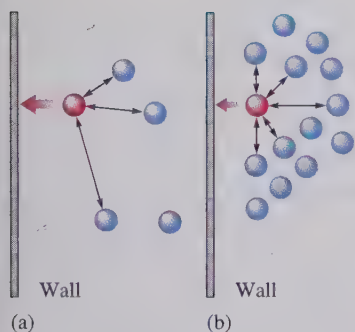


FIGURE 5.27

(a) Gas at low concentration—relatively few interactions between particles. The indicated gas particle exerts a pressure on the wall close to that predicted for an ideal gas. (b) Gas at high concentration—many more interactions between particles. The indicated gas particle exerts a much lower pressure on the wall than would be expected in the absence of interactions.

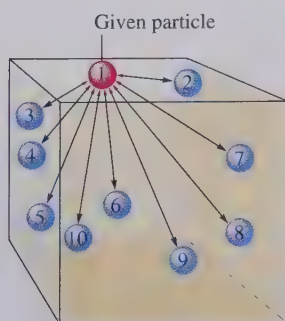


FIGURE 5.28

Illustration of pairwise interactions among gas particles. In a sample with 10 particles, each particle has 9 possible partners, to give $10(9)/2 = 45$ distinct pairs. The factor of $\frac{1}{2}$ arises because when particle 1 is the particle of interest we count the $1 \cdots 2$ pair, and when particle 2 is the particle of interest we count the $2 \cdots 1$ pair. However, $1 \cdots 2$ and $2 \cdots 1$ are the same pair that we have counted twice. Therefore, we must divide by 2 to get the actual number of pairs.

We have now corrected for both the finite volume and the attractive forces of the particles.

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Observed pressure
Volume of the container
Volume correction
Pressure correction

This equation can be rearranged to give the **van der Waals equation**:

P_{obs} is usually called just P .

$$\underbrace{\left[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2 \right]}_{P_{\text{ideal}}} \times \underbrace{(V - nb)}_{V_{\text{ideal}}} = nRT$$

Corrected pressure Corrected volume

The values of the weighting factors a and b are determined for a given gas by fitting experimental behavior. That is, a and b are varied until the best fit of the observed pressure is obtained under all conditions. The values of a and b for various gases are given in Table 5.3.

Experimental studies indicate that the changes van der Waals made in the basic assumptions of the kinetic molecular theory correct the major flaws in the model. First, consider the effects of volume. For a gas at low pressure (large volume), the volume of the container is very large compared with the volumes of the gas particles. That is, in this case the volume available to the gas is essentially equal to the volume of the container, and the gas behaves ideally. On the other hand, for a gas at high pressure (small container volume), the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume. These cases are illustrated in Fig. 5.29. Note from Table 5.3 that the volume correction constant b generally increases with the size of the gas molecule, which gives further support to these arguments.

The fact that a real gas tends to behave more ideally at high temperatures also can be explained in terms of the van der Waals model. At high temperatures the particles are moving so rapidly that the effects of interparticle interactions are not very important.

The corrections to the kinetic molecular theory that van der Waals found necessary to explain real gas behavior make physical sense, which makes us confident that we understand the fundamentals of gas behavior at the particle level. This is significant because so much important chemistry takes place in the gas phase. In fact, the mixture of gases called the atmosphere is vital to our existence. In the following section we consider some of the important reactions that occur in the atmosphere.

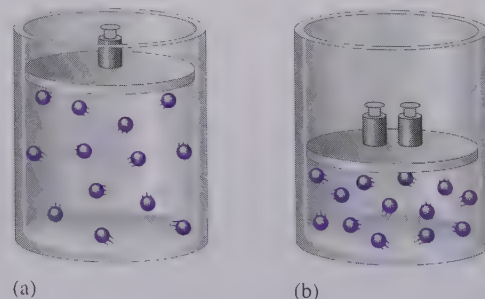
TABLE 5.3

Values of the van der Waals Constants for Some Common Gases

Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

FIGURE 5.29

The volume taken up by the gas particles themselves is less important at (a) large container volume (low pressure) than at (b) small container volume (high pressure).



5.9 Chemistry in the Atmosphere

TABLE 5.4
Atmospheric Composition
Near Sea Level (Dry Air)*

Component	Mole Fraction
N ₂	0.78084
O ₂	0.20948
Ar	0.00934
CO ₂	0.000345
Ne	0.00001818
He	0.00000524
CH ₄	0.00000168
Kr	0.00000114
H ₂	0.0000005
NO	0.0000005
Xe	0.000000087

*The atmosphere contains various amounts of water vapor depending on conditions.

The most important gases to us are those in the **atmosphere** that surrounds the earth's surface. The principal components are N₂ and O₂, but many other important gases, such as H₂O and CO₂, are also present. The average composition of the earth's atmosphere near sea level, with the water vapor removed, is shown in Table 5.4. Because of gravitational effects, the composition of the earth's atmosphere is not constant; heavier molecules tend to be near the earth's surface, and light molecules tend to migrate to higher altitudes, with some eventually escaping into space. The atmosphere is a highly complex and dynamic system, but for convenience we divide it into several layers based on the way the temperature changes with altitude. (The lowest layer, called the *troposphere*, is shown in Fig. 5.30.) Note that in contrast to the complex temperature profile of the atmosphere, the pressure decreases in a regular way with increasing altitude.

The chemistry occurring in the higher levels of the atmosphere is mostly determined by the effects of high-energy radiation and particles from the sun and other sources in space. In fact, the upper atmosphere serves as an important shield to prevent this high-energy radiation from reaching the earth, where it would damage the relatively fragile molecules sustaining life. In particular, the ozone in the upper atmosphere helps prevent high-energy ultraviolet radiation from penetrating to the earth. Intensive research is in progress to determine the natural factors that control the ozone concentration and how it is affected by chemicals released into the atmosphere.

The chemistry occurring in the troposphere, the layer of atmosphere closest to the earth's surface, is strongly influenced by human activities. Millions of tons of gases and particulates are released into the troposphere by our highly industrial civilization. Actually, it is amazing that the atmosphere can absorb so much material with relatively small permanent changes (so far).

Significant changes, however, are occurring. Severe **air pollution** is found around many large cities, and it is probable that long-range changes in our planet's weather are taking place. We will discuss some of the long-range effects of pollution in Chapter 6. In this section we will deal with short-term, localized effects of pollution.

The two main sources of pollution are transportation and the production of electricity. The combustion of petroleum in vehicles produces CO, CO₂, NO, and NO₂, along with unburned molecules from petroleum. When this mixture is trapped close to the ground in stagnant air, reactions occur producing chemicals that are potentially irritating and harmful to living systems.

The complex chemistry of polluted air appears to center around the nitrogen oxides (NO_x). At the high temperatures found in the gasoline and diesel engines of cars and trucks, N₂ and O₂ react to form

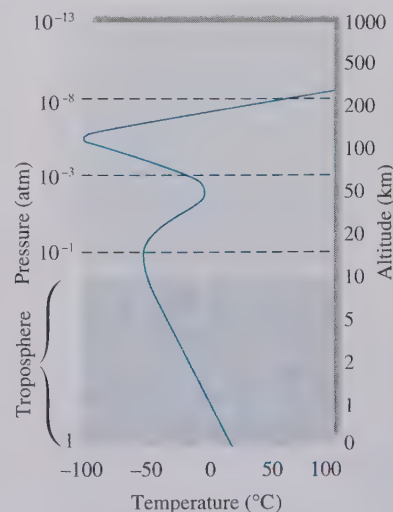


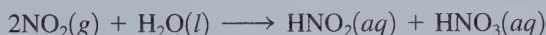
FIGURE 5.30
The variation of temperature (blue) and pressure (dashed lines) with altitude. Note that the pressure steadily decreases with altitude, but the temperature increases and decreases.

Acid Rain: A Growing Problem

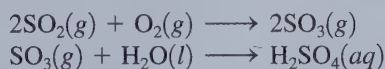
Rainwater, even in pristine wilderness areas, is slightly acidic because some of the carbon dioxide present in the atmosphere dissolves in the raindrops to produce H^+ ions by the following reaction:



This process produces only very small concentrations of H^+ ions in the rainwater. However, gases such as NO_2 and SO_2 , which are by-products of energy use, can produce significantly higher H^+ concentrations. Nitrogen dioxide reacts with water to give a mixture of nitrous acid and nitric acid:



Sulfur dioxide is oxidized to sulfur trioxide, which then reacts with water to form sulfuric acid:



The damage caused by the acid formed in polluted air is a growing worldwide problem. Lakes are dying in Nor-

way, the forests are under stress in Germany, and buildings and statues are deteriorating all over the world.

The Field Museum in Chicago contains more white Georgia marble than any other structure in the world. But nearly 70 years of exposure to the elements has taken such a toll on it that the building has recently undergone a multimillion-dollar renovation to replace the damaged marble with freshly quarried material.

What is the chemistry of the deterioration of marble by sulfuric acid? Marble is produced by geologic processes at high temperatures and pressures from limestone, a sedimentary rock formed by slow deposition of calcium carbonate from the shells of marine organisms. Limestone and marble are chemically identical (CaCO_3) but differ in physical properties; limestone is composed of smaller particles of calcium carbonate and is thus more porous and more workable. Although both limestone and marble are used for buildings, marble can be polished to a higher sheen and is often preferred for decorative purposes.

Both marble and limestone react with sulfuric acid to form calcium sulfate. The process can be represented most simply

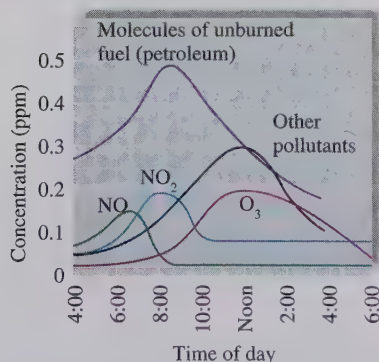
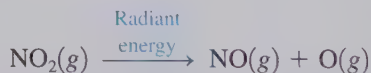


FIGURE 5.31 Concentration (in molecules per million molecules of "air") for some smog components versus time of day. (From "Photochemistry of Air Pollution," by P. A. Leighton, in *Physical Chemistry: A Series of Monographs*, edited by Eric Hutchinson and P. Van Rysseberghe, copyright 1961 and renewed 1989, Elsevier Science (USA), reproduced by permission of the publisher.)

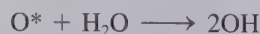
a small quantity of NO that is emitted into the air with the exhaust gases (see Fig. 5.31). This NO is immediately oxidized in air to NO_2 , which, in turn, absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atoms:



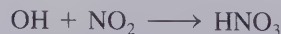
Oxygen atoms are very reactive and can combine with O_2 to form *ozone*:



Ozone is also very reactive and can react directly with other pollutants, or the ozone can absorb light and break up to form an energetically excited O_2 molecule (O_2^*) and an energetically excited oxygen atom (O^*). The latter species readily reacts with a water molecule to form two hydroxyl radicals (OH):



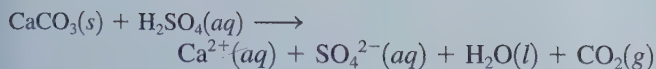
The hydroxyl radical is a very reactive oxidizing agent. For example, OH can react with NO_2 to form nitric acid:



The OH radical also can react with the unburned hydrocarbons in the polluted air to produce chemicals that cause the eyes to water and burn and are harmful to the respiratory system.

The OH radical has no charge [it has one fewer electron than the hydroxide ion (OH^-)].

as



In this equation the calcium sulfate is represented by separate hydrated ions because calcium sulfate is quite water soluble and dissolves in rainwater. Thus, in areas bathed by rainwater, the marble slowly dissolves away.

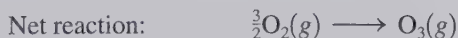
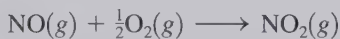
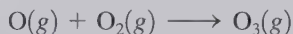
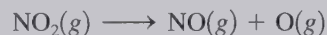
In areas of the building protected from the rain, the calcium sulfate can form the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The $\cdot 2\text{H}_2\text{O}$ in the formula of gypsum indicates the presence of two water molecules (called *waters of hydration*) for each CaSO_4 formula unit in the solid. The smooth surface of the marble is thus replaced by a thin layer of gypsum, a more porous material that binds soot and dust.

What can be done to protect limestone and marble structures from this kind of damage? Of course, one approach is to lower sulfur dioxide emissions from power plants (see Fig. 5.33). In addition, scientists are experimenting with coatings to protect marble from the acidic atmosphere. However, a coating can do more harm than good unless it “breathes.” If moisture trapped beneath the coating freezes, the expanding ice can fracture the marble. Needless to say, it is difficult to find a coating that will allow water, but not acid, to pass—but the search continues.



The damaging effects of acid rain can be seen by comparing these photos of a decorative statue on the Field Museum in Chicago. The first photo was taken about 1920, the second in 1990.

The end product of this whole process is often referred to as **photochemical smog**, so called because light is required to initiate some of the reactions. The production of photochemical smog can be understood more clearly by examining as a group the reactions discussed above:

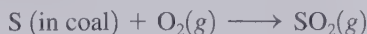


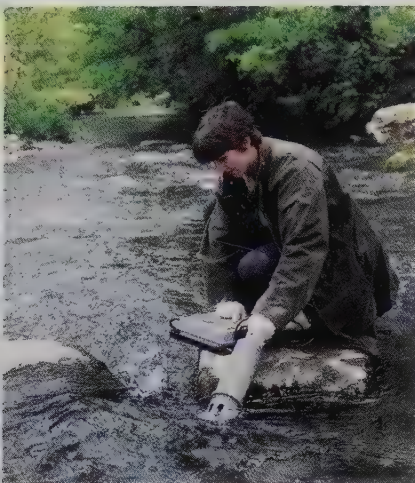
Although represented here as O_2 , the actual oxidant for NO is OH or an organic peroxide such as CH_3COO , formed by oxidation of organic pollutants.

Note that the NO_2 molecules assist in the formation of ozone without being themselves used up. The ozone formed then leads to the formation of OH and other pollutants.

We can observe this process by analyzing polluted air at various times during a day (see Fig. 5.31). As people drive to work between 6 and 8 a.m., the amounts of NO, NO_2 , and unburned molecules from petroleum increase. Later, as the decomposition of NO_2 occurs, the concentration of ozone and other pollutants builds up. Current efforts to combat the formation of photochemical smog are focused on cutting down the amounts of molecules from unburned fuel in automobile exhaust and designing engines that produce less nitric oxide.

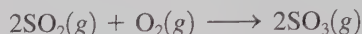
The other major source of pollution results from burning coal to produce electricity. Much of the coal found in the Midwest contains significant quantities of sulfur, which, when burned, produces sulfur dioxide:



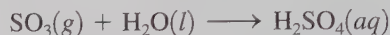
**FIGURE 5.32**

An environmental officer in Wales tests the pH of water.

A further oxidation reaction occurs when sulfur dioxide is changed to sulfur trioxide in the air:*



The production of sulfur trioxide is significant because it can combine with droplets of water in the air to form sulfuric acid:

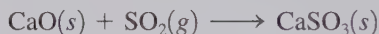


Sulfuric acid is very corrosive to both living things and building materials. Another result of this type of pollution is **acid rain**. In many parts of the northeastern United States and southeastern Canada, acid rain has caused some freshwater lakes to become too acidic to support any life (Fig. 5.32).

The problem of sulfur dioxide pollution is made more complicated by the energy crisis. As petroleum supplies dwindle and the price increases, our dependence on coal will probably grow. As supplies of low-sulfur coal are used up, high-sulfur coal will be utilized. One way to use high-sulfur coal without further harming the air quality is to remove the sulfur dioxide from the exhaust gas by means of a system called a *scrubber* before it is emitted from the power plant stack. A common method of scrubbing is to blow powdered limestone (CaCO_3) into the combustion chamber, where it is decomposed to lime and carbon dioxide:

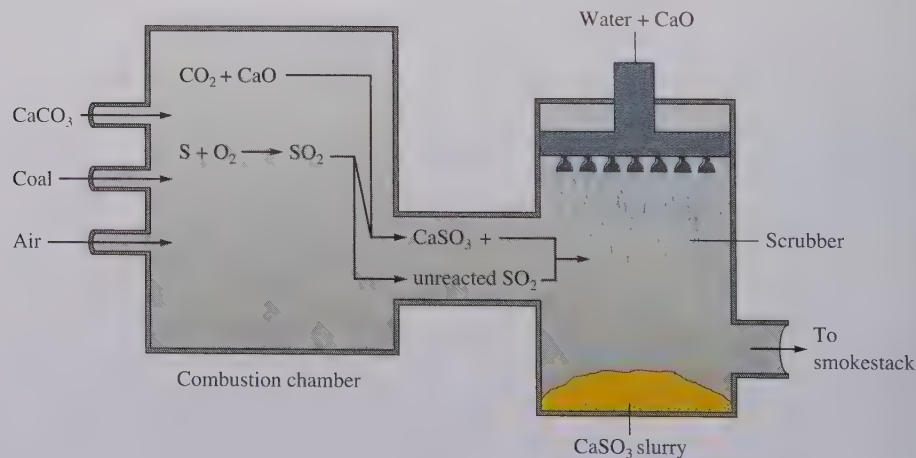


The lime then combines with the sulfur dioxide to form calcium sulfite:



To remove the calcium sulfite and any remaining unreacted sulfur dioxide, an aqueous suspension of lime is injected into the exhaust gases to produce a *slurry* (a thick suspension), as shown in Fig. 5.33.

Unfortunately, there are many problems associated with scrubbing. The systems are complicated and expensive and consume a great deal of energy. The large quantities of calcium sulfite produced in the process present a disposal problem. With a typical scrubber, approximately 1 ton of calcium sulfite per year is produced per

**FIGURE 5.33**

A schematic diagram of the process for scrubbing sulfur dioxide from stack gases in power plants.

*This reaction is very slow unless solid particles are present. See Chapter 12 for a discussion.

person served by the power plant. Since no use has yet been found for this calcium sulfite, it is usually buried in a landfill. As a result of these difficulties, air pollution by sulfur dioxide continues to be a major problem, one that is expensive in terms of damage to the environment and human health as well as in monetary terms.

For Review

Key Terms

Section 5.1

barometer
manometer
mm Hg
torr
standard atmosphere
pascal

Section 5.2

Boyle's law
ideal gas
Charles's law
absolute zero
Avogadro's law

Section 5.3

universal gas constant
ideal gas law

Section 5.4

molar volume
standard temperature and pressure (STP)

Section 5.5

Dalton's law of partial pressures
partial pressure
mole fraction

Section 5.6

kinetic molecular theory (KMT)
root mean square velocity
joule

Section 5.7

diffusion
effusion
Graham's law of effusion

Section 5.8

real gas
van der Waals equation

Section 5.9

atmosphere
air pollution
photochemical smog
acid rain

Summary

Of the three states of matter, the gaseous state is the most easily understood experimentally and theoretically. A gas can be described quantitatively by specifying four properties: volume, pressure, temperature, and the amount of gas present.

Atmospheric pressure is measured with a barometer, and in the laboratory, gas pressure is usually measured with a manometer. Both devices employ columns filled with mercury, and the most commonly used units of pressure are based on the height of such a column in millimeters: 1 mm Hg equals 1 torr; 1 standard atmosphere equals 760 torr. In the SI system, the unit of pressure is the pascal (1 N/m²).

Early experiments on the behavior of gases dealt with the relationship among the four characteristic properties. Boyle's law states that the volume of a given amount of a gas is inversely proportional to its pressure (at constant temperature). Charles's law states that for a given amount of gas at a constant pressure, the volume is directly proportional to the temperature in Kelvins. At a temperature of -273.2°C (0 K), the volume of a gas extrapolates to zero, and this temperature is called absolute zero. Avogadro's law states that equal volumes of gases at the same temperature and pressure contain the same number of particles.

These three laws can be combined into the ideal gas law:

$$PV = nRT$$

where R is called the universal gas constant ($0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$). This equation allows calculation of any one of the characteristic properties, given the other three. The ideal gas law describes the limiting behavior approached by real gases at low pressures and high temperatures.

The molar volume (22.42 liters) is the volume of an ideal gas at STP (standard temperature and pressure) or 0°C and 1 atmosphere.

The pressure of a gaseous mixture is described by Dalton's law of partial pressures, which states that the total pressure of a mixture of gases in a container is the sum of the pressures that each gas would exert if it were alone (its partial pressure), that is,

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots$$

The mole fraction of a given component in a mixture of gases can be calculated from the ratio of the partial pressure of that component to the total gas pressure.

The kinetic molecular theory of gases is a theoretical model constructed to account for ideal gas behavior. This model assumes that the volume of the gas particles is zero, that there are no interactions between particles, and that the particles are in constant motion, colliding with the container walls to produce pressure. In addition, this model shows that the average kinetic energy of the gas particles is directly proportional to the Kelvin temperature of the gas.

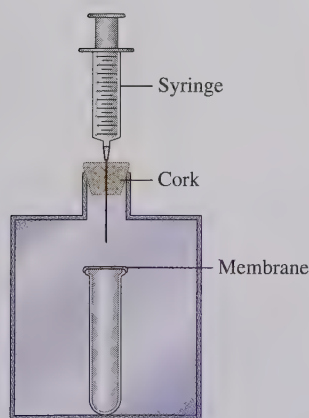
The root mean square velocity for the particles in a gas can be calculated from the temperature and the molar mass of the gas. Within any gas sample there is a range of velocities, since the gas particles collide and exchange kinetic energy. An increase in temperature increases the average velocity of the gas particles. The relative rates of diffusion, the mixing of gases, and effusion, the passage of a gas through a small orifice into an empty chamber, are inversely proportional to the square roots of the atomic or molar masses of the gases in question.

Real gases behave ideally only at high temperatures and low pressures. The van der Waals equation is a modification of the ideal gas equation that takes into consideration that real gas particles take up volume and interact with each other.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Consider the following apparatus: a test tube covered with a nonpermeable elastic membrane inside a container that is closed with a cork. A syringe goes through the cork. A syringe goes through the cork.

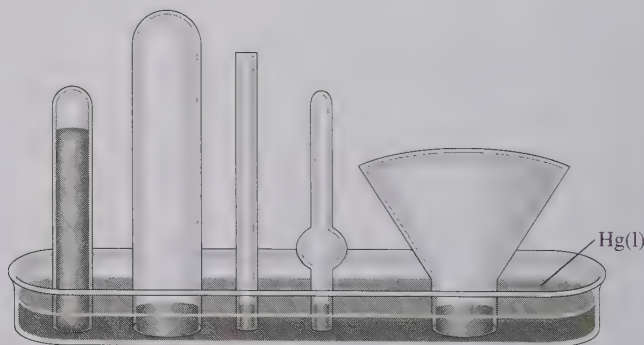


- a. As you push down on the syringe, how does the membrane covering the test tube change?
 - b. You stop pushing the syringe but continue to hold it down. In a few seconds, what happens to the membrane?
2. Figure 5.2 shows a picture of a barometer. Which of the following statements is the best explanation of how this barometer works?
 - a. Air pressure outside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
 - b. Air pressure inside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
 - c. Air pressure outside the tube counterbalances the weight of the mercury in the tube.

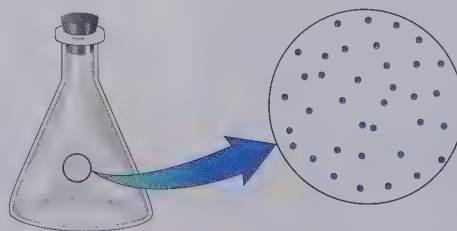
- d. Capillary action of the mercury causes the mercury to go up the tube.
- e. The vacuum that is formed at the top of the tube holds up the mercury.

Justify your choice, and for the choices you did not pick, explain what is wrong with them. Pictures help!

3. The barometer below shows the level of mercury at a given atmospheric pressure. Fill all the other barometers with mercury for that same atmospheric pressure. Explain your answer.



4. As you increase the temperature of a gas in a sealed, rigid container, what happens to the density of the gas? Would the results be the same if you did the same experiment in a container with a piston at constant pressure? (See Figure 5.17.)
5. A diagram in a chemistry book shows a magnified view of a flask of air as follows:



What do you suppose is between the dots (the dots represent air molecules)?

- air
 - dust
 - pollutants
 - oxygen
 - nothing
- If you put a drinking straw in water, place your finger over the opening, and lift the straw out of the water, some water stays in the straw. Explain.
 - A chemistry student relates the following story: I noticed my tires were a bit low and went to the gas station. As I was filling the tires, I thought about the kinetic molecular theory (KMT). I noticed the tires because the volume was low, and I realized that I was increasing both the pressure and volume of the tires. "Hmmm," I thought, "that goes against what I learned in chemistry, where I was told pressure and volume are inversely proportional." What is the fault in the logic of the chemistry student in this situation? Explain *why* we think pressure and volume to be inversely related (draw pictures and use the KMT).
 - Chemicals X and Y (both gases) react to form the gas XY , but it takes a bit of time for the reaction to occur. Both X and Y are placed in a container with a piston (free to move), and you note the volume. As the reaction occurs, what happens to the volume of the container? (See Fig. 5.18.)
 - Which statement best explains why a hot-air balloon rises when the air in the balloon is heated?
 - According to Charles's law, the temperature of a gas is directly related to its volume. Thus the volume of the balloon increases, making the density smaller. This lifts the balloon.
 - Hot air rises inside the balloon, and this lifts the balloon.
 - The temperature of a gas is directly related to its pressure. The pressure therefore increases, and this lifts the balloon.
 - Some of the gas escapes from the bottom of the balloon, thus decreasing the mass of gas in the balloon. This decreases the density of the gas in the balloon, which lifts the balloon.
 - Temperature is related to the root mean square velocity of the gas molecules. Thus the molecules are moving faster, hitting the balloon more, and thus lifting the balloon.
 Justify your choice, and for the choices you did not pick, explain what is wrong with them.
 - Draw a highly magnified view of a sealed, rigid container filled with a gas. Then draw what it would look like if you cooled the gas significantly but kept the temperature above the boiling point of the substance in the container. Also draw what it would look like if you heated the gas significantly. Finally, draw what each situation would look like if you evacuated enough of the gas to decrease the pressure by a factor of 2.
 - If you release a helium balloon, it soars upward and eventually pops. Explain this behavior.

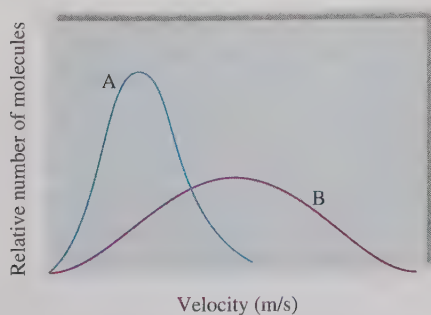
- If you have any two gases in different containers that are the same size at the same pressure and same temperature, what is true about the moles of each gas? Why is this true?
- Explain the following seeming contradiction: You have two gases, A and B , in two separate containers of equal volume and at equal pressure and temperature. Therefore, you must have the same number of moles of each gas. Because the two temperatures are equal, the average kinetic energies of the two samples are equal. Therefore, since the energy given such a system will be converted to translational motion (that is, move the molecules), the root mean square velocities of the two are equal, and thus the particles in each sample move, on average, with the same relative speed. Since A and B are different gases, they each must have a different molar mass. If A has higher molar mass than B , the particles of A must be hitting the sides of the container with more force. Thus the pressure in the container of gas A must be higher than that in the container with gas B . However, one of our initial assumptions was that the pressures were equal.
- You have a balloon covering the mouth of a flask filled with air at 1 atm. You apply heat to the bottom of the flask until the volume of the balloon is equal to that of the flask.
 - Which has more air in it, the balloon or the flask? Or do both have the same amount? Explain.
 - In which is the pressure greater, the balloon or the flask? Or is the pressure the same? Explain.
- How does Dalton's law of partial pressures help us with our model of ideal gases? That is, what postulates of the kinetic molecular theory does it support?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

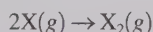
Questions

- Rationalize the following observations.
 - Aerosol cans will explode if heated.
 - You can drink through a soda straw.
 - A thin-walled can will collapse when the air inside is removed by a vacuum pump.
 - Manufacturers produce different types of tennis balls for high and low elevations.
- Show how Boyle's law and Charles's law are special cases of the ideal gas law.
- Using the postulates of the kinetic molecular theory, give molecular interpretations of Boyle's law and Charles's law.
- Why do real gases not always behave ideally? Under what conditions does a real gas behave most ideally? Why?
- At room temperature, water is a liquid with a molar volume of 18 mL. At 105°C and 1 atm pressure, water is a gas and has a molar volume of over 30 L. Explain the large difference in molar volumes.
- Briefly describe two methods one might use to find the molar mass of a newly synthesized gas for which a molecular formula was not known.

22. Consider the following velocity distribution curves A and B.

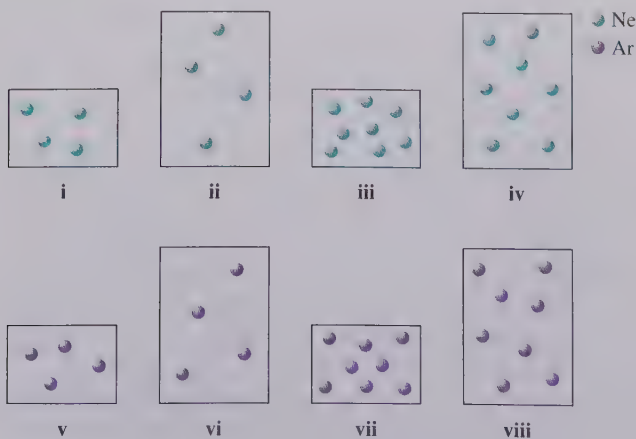


- If the plots represent the velocity distribution of 1.0 L of $\text{He}(g)$ at STP versus 1.0 L of $\text{Cl}_2(g)$ at STP, which plot corresponds to each gas? Explain your reasoning.
 - If the plots represent the velocity distribution of 1.0 L of $\text{O}_2(g)$ at temperatures of 273 K versus 1273 K, which plot corresponds to each temperature? Explain your reasoning. Under which temperature condition would the $\text{O}_2(g)$ sample behave most ideally? Explain.
23. Consider the following balanced equation in which gas X forms gas X_2 :



Equal moles of X are placed in two separate containers. One container is rigid so the volume cannot change; the other container is flexible so the volume changes to keep the internal pressure equal to the external pressure. The above reaction is run in each container. What happens to the pressure and density of the gas inside each container as reactants are converted to products?

24. Consider the following samples of gases at the same temperature.



Arrange each of these samples in order from lowest to highest:

- pressure
- average kinetic energy
- density
- root mean square velocity

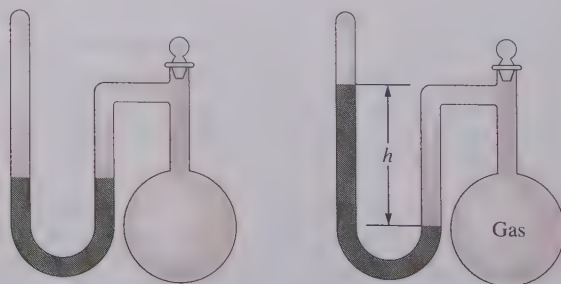
Note: Some samples of gases may have equal values for these attributes. Assume the larger containers have a volume twice the volume of the smaller containers and assume the mass of an argon atom is twice the mass of a neon atom.

Exercises

In this section similar exercises are paired.

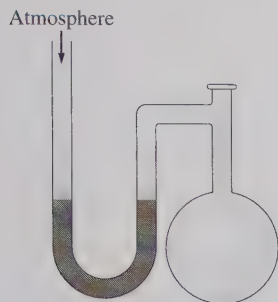
Pressure

- Freon-12 (CF_2Cl_2) is commonly used as the refrigerant in central home air conditioners. The system is initially charged to a pressure of 4.8 atm. Express this pressure in each of the following units (1 atm = 14.7 psi).
 - mm Hg
 - torr
 - Pa
 - psi
- A gauge on a compressed gas cylinder reads 2200 psi (pounds per square inch; 1 atm = 14.7 psi). Express this pressure in each of the following units.
 - standard atmospheres
 - megapascals (MPa)
 - torr
- A sealed-tube manometer (as shown below) can be used to measure pressures below atmospheric pressure. The tube above the mercury is evacuated. When there is a vacuum in the flask, the mercury levels in both arms of the U-tube are equal. If a gaseous sample is introduced into the flask, the mercury levels are different. The difference h is a measure of the pressure of the gas inside the flask. If h is equal to 6.5 cm, calculate the pressure in the flask in torr, pascals, and atmospheres.

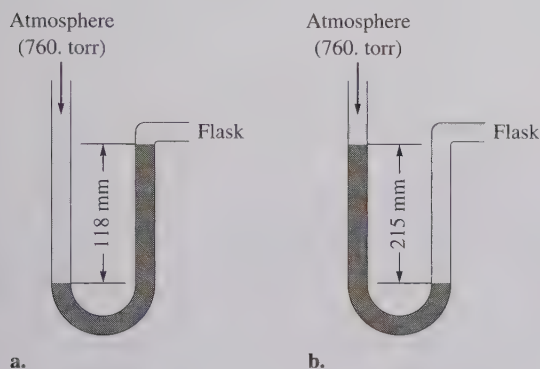


- If the sealed-tube manometer in Exercise 27 had a height difference of 20.0 inches between the mercury levels, what is the pressure in the flask in torr and atmospheres?

29. A diagram for an open-tube manometer is shown below.



If the flask is open to the atmosphere, the mercury levels are equal. For each of the following situations where a gas is contained in the flask, calculate the pressure in the flask in torr, atmospheres, and pascals.



- a. Calculate the pressures in the flask in parts a and b (in torr) if the atmospheric pressure is 635 torr.
30. a. If the open-tube manometer in Exercise 29 contains a nonvolatile silicone oil (density = 1.30 g/cm^3) instead of mercury (density = 13.6 g/cm^3), what are the pressures in the flask as shown in parts a and b in torr, atmospheres, and pascals?
- b. What advantage would there be in using a less dense fluid than mercury in a manometer used to measure relatively small differences in pressure?

Gas Laws

31. An aerosol can contains 400. mL of compressed gas at 5.20 atm pressure. When all the gas is sprayed into a large plastic bag, the bag inflates to a volume of 2.14 L. What is the pressure of gas inside the plastic bag? Assume temperature is constant.
32. A balloon is filled to a volume of $7.00 \times 10^2 \text{ mL}$ at a temperature of 20.0°C . The balloon is then cooled at constant pressure to a temperature of $1.00 \times 10^2 \text{ K}$. What is the final volume of the balloon?

33. If 0.500 mol of nitrogen gas occupies a volume of 11.2 L at 0°C , what volume will 2.00 mol of nitrogen gas occupy at the same temperature and pressure?
34. Consider the following chemical equation.



If 25.0 mL of NO_2 gas is completely converted to N_2O_4 gas under the same conditions, what volume will the N_2O_4 occupy?

35. Complete the following table for an ideal gas.

	P (atm)	V (L)	n (mol)	T
a.	5.00		2.00	155°C
b.	0.300	2.00		155 K
c.	4.47	25.0	2.01	
d.		2.25	10.5	75°C

36. Complete the following table for an ideal gas.

	P (atm)	V (L)	n (mol)	T
a.	$7.74 \times 10^3 \text{ Pa}$	12.2 mL		25°C
b.		43.0 mL	0.421 mol	223 K
c.	455 torr		$4.4 \times 10^{-2} \text{ mol}$	331°C
d.	745 mm Hg	11.2 L	0.401 mol	

37. Suppose two 200.0-L tanks are to be filled separately with the gases helium and hydrogen. What mass of each gas is needed to produce a pressure of 135 atm in its respective tank at 24°C ?
38. A 5.0-L flask contains 0.60 g O_2 at a temperature of 22°C . What is the pressure (in atm) inside the flask?
39. A 2.50-L container is filled with 175 g argon.
- If the pressure is 10.0 atm, what is the temperature?
 - If the temperature is 225 K, what is the pressure?
40. A person accidentally swallows a drop of liquid oxygen, $\text{O}_2(\text{l})$, which has a density of 1.149 g/mL . Assuming the drop has a volume of 0.050 mL, what volume of gas will be produced in the person's stomach at body temperature (37°C) and a pressure of 1.0 atm?
41. A particular balloon is designed by its manufacturer to be inflated to a volume of no more than 2.5 L. If the balloon is filled with 2.0 L of helium at sea level, is released, and rises to an altitude at which the atmospheric pressure is only 500. mm Hg, will the balloon burst? (Assume temperature is constant.)
42. A bicycle tire is filled with air to a pressure of 100. psi at a temperature of 19°C . Riding the bike on asphalt on a hot day increases the temperature of the tire to 58°C . The volume of

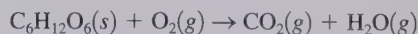
the tire increases by 4.0%. What is the new pressure in the bicycle tire?

43. A compressed gas cylinder, at 13.7 MPa and 23°C, is in a room where a fire raises the temperature to 450.°C. What is the new pressure in the cylinder?
44. A container is filled with an ideal gas to a pressure of 40.0 atm at 0°C.
- What will be the pressure in the container if it is heated to 45°C?
 - At what temperature would the pressure be 1.50×10^2 atm?
 - At what temperature would the pressure be 25.0 atm?
45. An ideal gas is contained in a cylinder with a volume of 5.0×10^2 mL at a temperature of 30.°C and a pressure of 710. torr. The gas is then compressed to a volume of 25 mL, and the temperature is raised to 820.°C. What is the new pressure of the gas?
46. A compressed gas cylinder contains 1.00×10^3 g of argon gas. The pressure inside the cylinder is 2050. psi (pounds per square inch) at a temperature of 18°C. How much gas remains in the cylinder if the pressure is decreased to 650. psi at a temperature of 26°C?

47. A sealed balloon is filled with 1.00 L of helium at 23°C and 1.00 atm. The balloon rises to a point in the atmosphere where the pressure is 220. torr and the temperature is -31°C. What is the change in volume of the balloon as it ascends from 1.00 atm to a pressure of 220. torr?
48. A hot-air balloon is filled with air to a volume of 4.00×10^3 m³ at 745 torr and 21°C. The air in the balloon is then heated to 62°C, causing the balloon to expand to a volume of 4.20×10^3 m³. What is the ratio of the number of moles of air in the heated balloon to the original number of moles of air in the balloon? (*Hint:* Openings in the balloon allow air to flow in and out. Thus the pressure in the balloon is always the same as that of the atmosphere.)

Gas Density, Molar Mass, and Reaction Stoichiometry

49. What mass of helium is required to fill a 1.5-L balloon at STP?
50. A student adds 4.00 g of dry ice (solid CO₂) to an empty balloon. What will be the volume of the balloon at STP after all the dry ice sublimates (converts to gaseous CO₂)?
51. Consider the following *unbalanced* chemical equation:



What volume of oxygen gas, measured at 28°C and 0.976 atm, is needed to react with 5.00 g of C₆H₁₂O₆? What volume of each product is produced under the same conditions?

52. Concentrated hydrogen peroxide solutions are explosively decomposed by traces of transition metal ions (such as Mn or Fe):



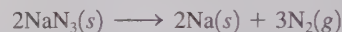
What volume of pure O₂(g), collected at 27°C and 746 torr, would be generated by decomposition of 125 g of a 50.0% by mass hydrogen peroxide solution? Ignore any water vapor that may be present.

53. In 1897 the Swedish explorer Andréé tried to reach the North Pole in a balloon. The balloon was filled with hydrogen gas. The hydrogen gas was prepared from iron splints and diluted sulfuric acid. The reaction is



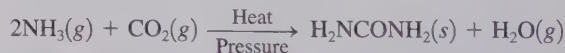
The volume of the balloon was 4800 m³ and the loss of hydrogen gas during filling was estimated at 20.%. What mass of iron splints and 98% (by mass) H₂SO₄ were needed to ensure the complete filling of the balloon? Assume a temperature of 0°C, a pressure of 1.0 atm during filling, and 100% yield.

54. Air bags are activated when a severe impact causes a steel ball to compress a spring and electrically ignite a detonator cap. This causes sodium azide (NaN₃) to decompose explosively according to the following reaction:



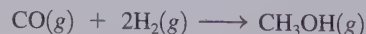
What mass of NaN₃(s) must be reacted to inflate an air bag to 70.0 L at STP?

55. Consider the reaction between 50.0 mL of liquid methyl alcohol, CH₃OH (density = 0.850 g/mL), and 22.8 L of O₂ at 27°C and a pressure of 2.00 atm. The products of the reaction are CO₂(g) and H₂O(g). Calculate the number of moles of H₂O formed if the reaction goes to completion.
56. Urea (H₂NCONH₂) is used extensively as a nitrogen source in fertilizers. It is produced commercially from the reaction of ammonia and carbon dioxide:



Ammonia gas at 223°C and 90. atm flows into a reactor at a rate of 500. L/min. Carbon dioxide at 223°C and 45 atm flows into the reactor at a rate of 600. L/min. What mass of urea is produced per minute by this reaction assuming 100% yield?

57. Hydrogen cyanide is prepared commercially by the reaction of methane, CH₄(g), ammonia, NH₃(g), and oxygen, O₂(g), at high temperature. The other product is gaseous water.
- Write a chemical equation for the reaction.
 - What volume of HCN(g) can be obtained from 20.0 L CH₄(g), 20.0 L NH₃(g), and 20.0 L O₂(g)? The volumes of all gases are measured at the same temperature and pressure.
58. Methanol, CH₃OH, can be produced by the following reaction:

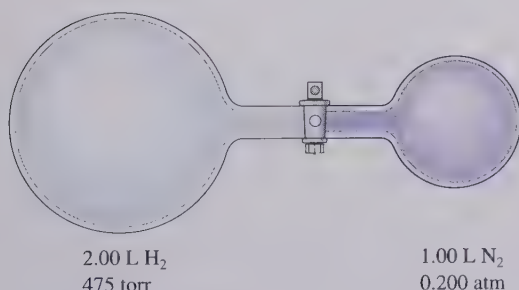


Hydrogen at STP flows into a reactor at a rate of 16.0 L/min. Carbon monoxide at STP flows into the reactor at a rate of 25.0 L/min. If 5.30 g of methanol is produced per minute, what is the percent yield of the reaction?

59. A gas consisting of only carbon and hydrogen has an empirical formula of CH_2 . The gas has a density of 1.65 g/L at 27°C and 734 torr. Determine the molar mass and molecular formula of the gas.
60. A compound has the empirical formula CHCl . A 256-mL flask, at 373 K and 750. torr, contains 0.800 g of the gaseous compound. Give the molecular formula.
61. Silicon tetrachloride (SiCl_4) and trichlorosilane (SiHCl_3) are both starting materials for the production of electronics-grade silicon. Calculate the densities of pure SiCl_4 and pure SiHCl_3 vapor at 85°C and 758 torr.
62. Uranium hexafluoride is a solid at room temperature, but it boils at 56°C . Determine the density of uranium hexafluoride at 60°C and 745 torr.

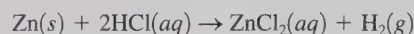
Partial Pressure

63. A piece of solid carbon dioxide, with a mass of 7.8 g, is placed in a 4.0-L otherwise empty container at 27°C . What is the pressure in the container after all the carbon dioxide vaporizes? If 7.8 g solid carbon dioxide were placed in the same container but it already contained air at 740 torr, what would be the partial pressure of carbon dioxide and the total pressure in the container after the carbon dioxide vaporizes?
64. A mixture of 1.00 g H_2 and 1.00 g He is placed in a 1.00-L container at 27°C . Calculate the partial pressure of each gas and the total pressure.
65. Consider the flasks in the following diagram. What are the final partial pressures of H_2 and N_2 after the stopcock between the two flasks is opened? (Assume the final volume is 3.00 L.) What is the total pressure (in torr)?



66. Consider the flask apparatus in Exercise 65, which contains 2.00 L of H_2 at a pressure of 360. torr and 1.00 L of N_2 at an unknown pressure. If the total pressure in the flasks is 320. torr after the stopcock is opened, determine the initial pressure of N_2 in the 1.00-L flask.

67. The partial pressure of $\text{CH}_4(\text{g})$ is 0.175 atm and that of $\text{O}_2(\text{g})$ is 0.250 atm in a mixture of the two gases.
- What is the mole fraction of each gas in the mixture?
 - If the mixture occupies a volume of 10.5 L at 65°C , calculate the total number of moles of gas in the mixture.
 - Calculate the number of grams of each gas in the mixture.
68. A 1.00-L gas sample at 100°C and 600. torr contains 50.0% helium and 50.0% xenon by mass. What are the partial pressures of the individual gases?
69. Small quantities of hydrogen gas can be prepared in the laboratory by the addition of aqueous hydrochloric acid to metallic zinc.



Typically, the hydrogen gas is bubbled through water for collection and becomes saturated with water vapor. Suppose 240. mL of hydrogen gas is collected at 30°C and has a total pressure of 1.032 atm by this process. What is the partial pressure of hydrogen gas in the sample? How many grams of zinc must have reacted to produce this quantity of hydrogen? (The vapor pressure of water is 32 torr at 30°C .)

70. Helium is collected over water at 25°C and 1.00 atm total pressure. What total volume of gas must be collected to obtain 0.586 g of helium? (At 25°C the vapor pressure of water is 23.8 torr.)
71. At elevated temperatures, sodium chlorate decomposes to produce sodium chloride and oxygen gas. A 0.8765-g sample of impure sodium chlorate was heated until the production of oxygen gas ceased. The oxygen gas collected over water occupied 57.2 mL at a temperature of 22°C and a pressure of 734 torr. Calculate the mass percent of NaClO_3 in the original sample. (At 22°C the vapor pressure of water is 19.8 torr.)
72. Xenon and fluorine will react to form binary compounds when a mixture of these two gases is heated to 400°C in a nickel reaction vessel. A 100.0-mL nickel container is filled with xenon and fluorine, giving partial pressures of 1.24 atm and 10.10 atm, respectively, at a temperature of 25°C . The reaction vessel is heated to 400°C to cause a reaction to occur and then cooled to a temperature at which F_2 is a gas and the xenon fluoride compound produced is a non-volatile solid. The remaining F_2 gas is transferred to another 100.0-mL nickel container, where the pressure of F_2 at 25°C is 7.62 atm. Assuming all of the xenon has reacted, what is the formula of the product?

Kinetic Molecular Theory and Real Gases

73. Calculate the average kinetic energy of the CH_4 molecules in a sample of CH_4 gas at 273 K and at 546 K.
74. Calculate the average kinetic energy of the N_2 molecules in a sample of N_2 gas at 273 K and at 546 K.
75. Calculate the root mean square velocity of the CH_4 molecules in a sample of CH_4 gas at 273 K and at 546 K.

Calculate the root mean square velocity of the N_2 molecules in a sample of N_2 gas at 273 K and at 546 K.

76. Consider separate 1.0-L samples of $\text{He}(g)$ and $\text{UF}_6(g)$, both at 1.00 atm and containing the same number of moles. What ratio of temperatures for the two samples would produce the same root mean square velocity?
77. Consider a 1-mol sample of $\text{CH}_4(g)$ at 273 K. If the temperature is increased, what happens to the average kinetic energy and the average velocity of the CH_4 molecules? Explain.
78. Consider a 1.0-L container of neon gas at STP. Will the average kinetic energy, average velocity, and frequency of collisions of gas molecules with the walls of the container increase, decrease, or remain the same under each of the following conditions?
- The temperature is increased to 100°C .
 - The temperature is decreased to -50°C .
 - The volume is decreased to 0.5 L.
 - The number of moles of neon is doubled.

79. Consider three identical flasks filled with different gases.

Flask A: CO at 760 torr and 0°C

Flask B: N_2 at 250 torr and 0°C

Flask C: H_2 at 100 torr and 0°C

- In which flask will the molecules have the greatest average kinetic energy?
 - In which flask will the molecules have the greatest average velocity?
80. Consider separate 1.0-L gaseous samples of H_2 , Xe, Cl_2 , and O_2 all at STP.
- Rank the gases in order of increasing average kinetic energy.
 - Rank the gases in order of increasing average velocity.
 - How can separate 1.0-L samples of O_2 and H_2 each have the same average velocity?
81. The effusion rate of an unknown gas is measured and found to be 31.50 mL/min. Under identical experimental conditions, the effusion rate of O_2 is found to be 30.50 mL/min. If the choices are CH_4 , CO, NO, CO_2 , and NO_2 , what is the identity of the unknown gas?
82. The rate of effusion of a particular gas was measured and found to be 24.0 mL/min. Under the same conditions, the rate of effusion of pure methane (CH_4) gas is 47.8 mL/min. What is the molar mass of the unknown gas?
83. One way of separating oxygen isotopes is by gaseous diffusion of carbon monoxide. The gaseous diffusion process behaves like an effusion process. Calculate the relative rates of effusion of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$. Name some advantages and disadvantages of separating oxygen isotopes by gaseous diffusion of carbon dioxide instead of carbon monoxide.
84. It took 4.5 minutes for 1.0 L helium to effuse through a porous barrier. How long will it take for 1.0 L Cl_2 gas to effuse under identical conditions?
85. Calculate the pressure exerted by 0.5000 mol N_2 in a 1.0000-L container at 25.0°C

- using the ideal gas law.
- using the van der Waals equation.
- Compare the results.

86. Calculate the pressure exerted by 0.5000 mol N_2 in a 10.000-L container at 25.0°C
- using the ideal gas law.
 - using the van der Waals equation.
 - Compare the results.
 - Compare the results with those in Exercise 85.

Atmosphere Chemistry

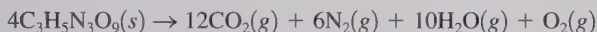
87. Use the data in Table 5.4 to calculate the partial pressure of NO in dry air assuming that the total pressure is 1.0 atm. Assuming a temperature of 0°C , calculate the number of molecules of NO per cubic centimeter.
88. Use the data in Table 5.4 to calculate the partial pressure of He in dry air assuming that the total pressure is 1.0 atm. Assuming a temperature of 25°C , calculate the number of He atoms per cubic centimeter.
89. A 10.0-L sample of air was collected at an altitude of 1.00×10^2 km. Estimate the volume of the sample at STP. (See Fig. 5.30.)
90. A 1.0-L sample of air is collected at 25°C at sea level (1.00 atm). Estimate the volume this sample of air would have at an altitude of 15 km (see Fig. 5.30).
91. Write reactions to show how nitric and sulfuric acids are produced in the atmosphere.
92. Write reactions to show how the nitric and sulfuric acids in acid rain react with marble and limestone. (Both marble and limestone are primarily calcium carbonate.)

Additional Exercises

93. Draw a qualitative graph to show how the first property varies with the second in each of the following (assume 1 mol of an ideal gas and T in Kelvin).
- PV versus V with constant T
 - P versus T with constant V
 - T versus V with constant P
 - P versus V with constant T
 - P versus $1/V$ with constant T
 - PV/T versus P
94. At STP, 1.0 L Br_2 reacts completely with 3.0 L F_2 , producing 2.0 L of a product. What is the formula of the product? (All substances are gases.)
95. A 2.747-g sample of manganese metal is reacted with excess HCl gas to produce 3.22 L of $\text{H}_2(g)$ at 373 K and 0.951 atm and a manganese chloride compound (MnCl_x). What is the formula of the manganese chloride compound produced in the reaction?
96. Equal moles of hydrogen gas and oxygen gas are mixed in a flexible reaction vessel and then sparked to initiate the formation of gaseous water. Assuming that the reaction

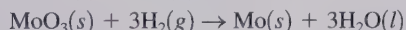
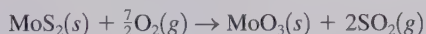
goes to completion, what is the ratio of the final volume of the gas mixture to the initial volume of the gas mixture if both volumes are measured at the same temperature and pressure?

97. A 15.0-L tank is filled with H_2 to a pressure of 2.00×10^2 atm. How many balloons (each 2.00 L) can be inflated to a pressure of 1.00 atm from the tank? Assume that there is no temperature change and that the tank cannot be emptied below 1.00 atm pressure.
98. A spherical glass container of unknown volume contains helium gas at 25°C and 1.960 atm. When a portion of the helium is withdrawn and adjusted to 1.00 atm at 25°C , it is found to have a volume of 1.75 cm^3 . The gas remaining in the first container shows a pressure of 1.710 atm. Calculate the volume of the spherical container.
99. A 2.00-L sample of $\text{O}_2(\text{g})$ was collected over water at a total pressure of 785 torr and 25°C . When the $\text{O}_2(\text{g})$ was dried (water vapor removed), the gas had a volume of 1.94 L at 25°C and 785 torr. Calculate the vapor pressure of water at 25°C .
100. Explosives are effective if they produce a large number of gaseous molecules as products. Nitroglycerin, for example, detonates according to the following equation:



If 25.0 g of nitroglycerin explodes in a 10.0-L rigid container, calculate the total pressure of all gases present assuming the temperature is $500.^\circ\text{C}$.

101. Metallic molybdenum can be produced from the mineral molybdenite, MoS_2 . The mineral is first oxidized in air to molybdenum trioxide and sulfur dioxide. Molybdenum trioxide is then reduced to metallic molybdenum using hydrogen gas. The balanced equations are

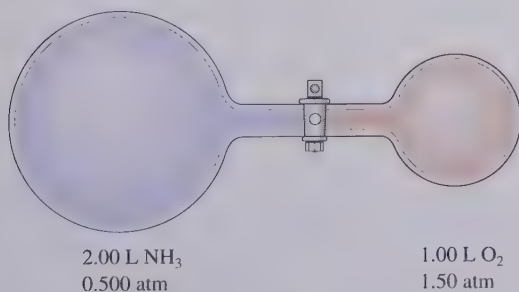


Calculate the volumes of air and hydrogen gas at 17°C and 1.00 atm that are necessary to produce 1.00×10^3 kg of pure molybdenum from MoS_2 . Assume air contains 21% oxygen by volume and assume 100% yield for each reaction.

102. Nitric acid is produced commercially by the Ostwald process. In the first step ammonia is oxidized to nitric oxide:



Assume this reaction is carried out in the apparatus diagramed below.



The stopcock between the two reaction containers is opened, and the reaction proceeds using proper catalysts. Calculate the partial pressure of NO after the reaction is complete. Assume 100% yield for the reaction, assume the final container volume is 3.00 L, and assume the temperature is constant.

103. In the "Méthode Champenoise," grape juice is fermented in a wine bottle to produce sparkling wine. The reaction is



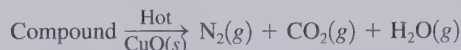
Fermentation of 750. mL grape juice (density = 1.0 g/cm^3) is allowed to take place in a bottle with a total volume of 825 mL until 12% by volume is ethanol ($\text{C}_2\text{H}_5\text{OH}$). Assuming that the CO_2 is insoluble in H_2O (actually, a wrong assumption), what would be the pressure of CO_2 inside the wine bottle at 25°C ? (The density of ethanol is 0.79 g/cm^3 .)

104. A 20.0-L stainless steel container was charged with 2.00 atm of hydrogen gas and 3.00 atm of oxygen gas. A spark ignited the mixture, producing water. What is the pressure in the tank at 25°C ? at 125°C ?
105. One of the chemical controversies of the nineteenth century concerned the element beryllium (Be). Berzelius originally claimed that beryllium was a trivalent element (forming Be^{3+} ions) and that it gave an oxide with the formula Be_2O_3 . This resulted in a calculated atomic mass of 13.5 for beryllium. In formulating his periodic table, Mendeleev proposed that beryllium was divalent (forming Be^{2+} ions) and that it gave an oxide with the formula BeO . This assumption gives an atomic mass of 9.0. In 1894, A. Combes (*Comptes Rendus* 1894, p. 1221) reacted beryllium with the anion $\text{C}_5\text{H}_7\text{O}_2^-$ and measured the density of the gaseous product. Combes's data for two different experiments are as follows:

	I	II
Mass	0.2022 g	0.2224 g
Volume	22.6 cm^3	26.0 cm^3
Temperature	13°C	17°C
Pressure	765.2 mm Hg	764.6 mm

If beryllium is a divalent metal, the molecular formula of the product will be $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$; if it is trivalent, the formula will be $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$. Show how Combes's data help to confirm that beryllium is a divalent metal.

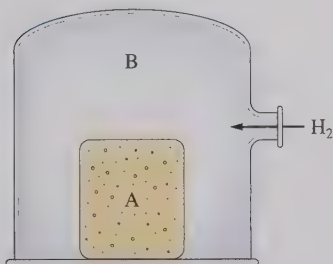
106. A compound contains only C, H, and N. It is 58.51% C and 7.37% H by mass. Helium effuses through a porous frit 3.20 times as fast as the compound does. Determine the empirical and molecular formulas of this compound.
107. The nitrogen content of organic compounds can be determined by the Dumas method. The compound in question is first reacted by passage over hot $\text{CuO}(\text{s})$:



The product gas is then passed through a concentrated solution of KOH to remove the CO_2 . After passage through the KOH solution, the gas contains N_2 and is saturated with

water vapor. In a given experiment a 0.253-g sample of a compound produced 31.8 mL N_2 saturated with water vapor at 25°C and 726 torr. What is the mass percent of nitrogen in the compound? (The vapor pressure of water at 25°C is 23.8 torr.)

108. An organic compound contains C, H, N, and O. Combustion of 0.1023 g of the compound in excess oxygen yielded 0.2766 g of CO_2 and 0.0991 g of H_2O . A sample of 0.4831 g of the compound was analyzed for nitrogen by the Dumas method (see Exercise 107). At STP, 27.6 mL of dry N_2 was obtained. In a third experiment, the density of the compound as a gas was found to be 4.02 g/L at 127°C and 256 torr. What are the empirical and molecular formulas of the compound?
109. Consider the following diagram:

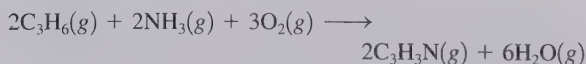


Container A (with porous walls) is filled with air at STP. It is then inserted into a large enclosed container (B), which is then flushed with $\text{H}_2(\text{g})$. What will happen to the pressure inside container A? Explain your answer.

110. Without looking at tables of values, which of the following gases would you expect to have the largest value of the van der Waals constant b : H_2 , N_2 , CH_4 , C_2H_6 , or C_3H_8 ?
111. From the values in Table 5.3 for the van der Waals constant a for the gases H_2 , CO_2 , N_2 , and CH_4 , predict which of these gas molecules show the strongest intermolecular attractions.

Challenge Problems

112. An important process for the production of acrylonitrile ($\text{C}_3\text{H}_3\text{N}$) is given by the following reaction:



A 150.-L reactor is charged to the following partial pressures at 25°C :

$$P_{\text{C}_3\text{H}_6} = 0.500 \text{ MPa}$$

$$P_{\text{NH}_3} = 0.800 \text{ MPa}$$

$$P_{\text{O}_2} = 1.500 \text{ MPa}$$

What mass of acrylonitrile can be produced from this mixture ($\text{MPa} = 10^6 \text{ Pa}$)?

113. A chemist weighed out 5.14 g of a mixture containing unknown amounts of $\text{BaO}(\text{s})$ and $\text{CaO}(\text{s})$ and placed the sample in a 1.50-L flask containing $\text{CO}_2(\text{g})$ at 30.0°C and 750.

torr. After the reaction to form $\text{BaCO}_3(\text{s})$ and $\text{CaCO}_3(\text{s})$ was completed, the pressure of $\text{CO}_2(\text{g})$ remaining was 230. torr. Calculate the mass percentages of $\text{CaO}(\text{s})$ and $\text{BaO}(\text{s})$ in the mixture.

114. A mixture of chromium and zinc weighing 0.362 g was reacted with an excess of hydrochloric acid. After all the metals in the mixture reacted, 225 mL of dry hydrogen gas was collected at 27°C and 750. torr. Determine the mass percent Zn in the metal sample. [Zinc reacts with hydrochloric acid to produce zinc chloride and hydrogen gas; chromium reacts with hydrochloric acid to produce chromium(III) chloride and hydrogen gas.]
115. Methane (CH_4) gas flows into a combustion chamber at a rate of 200. L/min at 1.50 atm and ambient temperature. Air is added to the chamber at 1.00 atm and the same temperature, and the gases are ignited.
- To ensure complete combustion of CH_4 to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, three times as much oxygen as is necessary is reacted. Assuming air is 21 mole percent O_2 and 79 mole percent N_2 , calculate the flow rate of air necessary to deliver the required amount of oxygen.
 - Under the conditions in part a, combustion of methane was not complete as a mixture of $\text{CO}_2(\text{g})$ and $\text{CO}(\text{g})$ was produced. It was determined that 95.0% of the carbon in the exhaust gas was present in CO_2 . The remainder was present as carbon in CO . Calculate the composition of the exhaust gas in terms of mole fraction of CO , CO_2 , O_2 , N_2 , and H_2O . Assume CH_4 is completely reacted and N_2 is unreacted.
116. A steel cylinder contains 5.00 mol of graphite (pure carbon) and 5.00 mol of O_2 . The mixture is ignited and all the graphite reacts. Combustion produces a mixture of CO gas and CO_2 gas. After the cylinder has cooled to its original temperature, it is found that the pressure of the cylinder has increased by 17.0%. Calculate the mole fractions of CO , CO_2 , and O_2 in the final gaseous mixture.
117. The total mass that can be lifted by a balloon is given by the difference between the mass of air displaced by the balloon and the mass of the gas inside the balloon. Consider a hot-air balloon that approximates a sphere 5.00 m in diameter and contains air heated to 65°C . The surrounding air temperature is 21°C . The pressure in the balloon is equal to the atmospheric pressure, which is 745 torr.
- What total mass can the balloon lift? Assume that the average molar mass of air is 29.0 g/mol. (Hint: Heated air is less dense than cool air.)
 - If the balloon is filled with enough helium at 21°C and 745 torr to achieve the same volume as in part a, what total mass can the balloon lift?
 - What mass could the hot-air balloon in part a lift if it were on the ground in Denver, Colorado, where a typical atmospheric pressure is 630. torr?
118. We state that the ideal gas law tends to hold best at low pressures and high temperatures. Show how the van der Waals equation simplifies to the ideal gas law under these conditions.

119. Atmospheric scientists often use mixing ratios to express the concentrations of trace compounds in air. Mixing ratios are often expressed as ppmv (parts per million volume):

$$\text{ppmv of } X = \frac{\text{vol. of } X \text{ at STP}}{\text{total vol. of air at STP}} \times 10^6$$

On a recent autumn day, the concentration of carbon monoxide in the air in downtown Denver, Colorado, reached 3.0×10^2 ppmv. The atmospheric pressure at that time was 628 torr, and the temperature was 0°C .

- What was the partial pressure of CO ?
 - What was the concentration of CO in molecules per cubic centimeter?
120. Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to form ammonia gas (NH_3). You have nitrogen and hydrogen gases in a 15.0-L container fitted with a movable piston (the piston allows the container volume to change so as to keep the pressure constant inside the container). Initially the partial pressure of each reactant gas is 1.00 atm. Assume the temperature is constant and that the reaction goes to completion.
- Calculate the partial pressure of ammonia in the container after the reaction has reached completion.
 - Calculate the volume of the container after the reaction has reached completion.

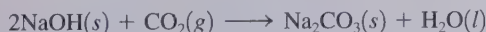
Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

121. Use the following information to identify element A and compound B, then answer questions a and b.

An empty glass container has a mass of 658.572 g. It has a mass of 659.452 g after it has been filled with nitrogen gas at a pressure of 790. torr and a temperature of 15°C . When the container is evacuated and refilled with a certain element (A) at a pressure of 745 torr and a temperature of 26°C , it has a mass of 660.59 g.

Compound B, a gaseous organic compound that consists of 85.6% carbon and 14.4% hydrogen by mass, is placed in a stainless steel vessel (10.68 L) with excess oxygen gas. The vessel is placed in a constant-temperature bath at 22°C . The pressure in the vessel is 11.98 atm. In the bottom of the vessel is a container that is packed with Ascarite and a desiccant. Ascarite is asbestos impregnated with sodium hydroxide; it quantitatively absorbs carbon dioxide:



The desiccant is anhydrous magnesium perchlorate, which quantitatively absorbs the water produced by the combustion reaction as well as the water produced by the above reaction. Neither the Ascarite nor the desiccant reacts with compound B or oxygen. The total mass of the container with the Ascarite and desiccant is 765.3 g.

The combustion reaction of compound B is initiated by a spark. The pressure immediately rises, then begins to decrease, and finally reaches a steady value of 6.02 atm. The stainless steel vessel is carefully opened, and the mass of the container inside the vessel is found to be 846.7 g.

A and B react quantitatively in a 1:1 mole ratio to form one mole of the single product, gas C.

- How many grams of C will be produced if 10.0 L of A and 8.60 L of B (each at STP) are reacted by opening a stopcock connecting the two samples?
- What will be the total pressure in the system?



Media Activities

- Boyle, Charles, and Avogadro studied the relationship between two variables of a gas while keeping the other two variables that affect gases constant. Which variables are studied and which variables are constant for Boyle's law, Charles's law, and Avogadro's law? Check your answers by playing the Boyle's Law and Charles's Law Visualizations on the student CD. Boyle's law can be depicted graphically in a few ways other than V vs. $1/P$. What does a plot of P versus V look like? PV versus P ? How does each plot illustrate the inverse relationship between pressure and volume of a gas at constant moles and temperature?
- Play the Liquid Nitrogen and Balloons Visualization on the student CD. In terms of the force of collisions per unit area, explain why the balloon collapsed when liquid N_2 was poured on the balloon. Why did the balloon return to its original shape at the end of the video?
- Play the Ideal Gas Law, $PV = nRT$ Visualization to review the relationships between P , V , n , and T . For each experiment, explain why the relationship is true in terms of the force of collisions per unit area.
- Play the Collapsing Can Visualization on the student CD. Assuming only $\text{H}_2\text{O}(g)$ is in the can, what is the pressure of water vapor inside the can before the can is stoppered? When the can is immersed in water, what happens to the temperature of the gas molecules inside the can? What happens to the moles of gas molecules inside the can as the can is immersed? What effect does this have on P_{inside} ? Put all these ideas together and explain why the can collapsed when it was immersed in water.
- What is diffusion? What is effusion? How is effusion of a gas related to the average velocity of the gas? to the molar mass of the gas? Check your answers by playing the Diffusion of Gases and the Effusion of a Gas Visualization on the student CD. In terms of molar mass and average velocity, why did the $\text{NH}_3(g)$ and $\text{HCl}(g)$ molecules meet on the HCl side of the tube?

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Thermochemistry

6

Energy is the essence of our very existence as individuals and as a society. The food that we eat furnishes the energy to live, work, and play, just as the coal and oil consumed by manufacturing and transportation systems power our modern industrialized civilization.

In the past, huge quantities of carbon-based fossil fuels have been available for the taking. This abundance of fuels has led to a world society with a voracious appetite for energy, consuming millions of barrels of petroleum every day. We are now dangerously dependent on the dwindling supplies of oil, and this dependence is an important source of tension among nations in today's world. In an incredibly short time we have moved from a period of ample and cheap supplies of petroleum to one of high prices and uncertain supplies. If our present standard of living is to be maintained, we must find alternatives to petroleum. To do this, we need to know the relationship between chemistry and energy, which we explore in this chapter.

There are additional problems with fossil fuels. The waste products from burning fossil fuels significantly affect our environment. For example, when a carbon-based fuel is burned, the carbon reacts with oxygen to form carbon dioxide, which is released into the atmosphere. Although much of this carbon dioxide is consumed in various natural processes such as photosynthesis and the formation of carbonate materials, the amount of carbon dioxide in the atmosphere is steadily increasing. This increase is significant because atmospheric carbon dioxide absorbs heat radiated from the earth's surface and radiates it back toward the earth. Since this is an important mechanism for controlling the earth's temperature, many scientists fear that an increase in the concentration of carbon dioxide will warm the earth, causing significant changes in climate. In addition, impurities in the fossil fuels react with components of the air to produce air pollution. We discussed some aspects of this problem in Chapter 5.

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- 6.1 The Nature of Energy**
 - Chemical Energy
- 6.2 Enthalpy and Calorimetry**
 - Enthalpy
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- 6.3 Hess's Law**
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- 6.4 Standard Enthalpies of Formation**
- 6.5 Present Sources of Energy**
 - Petroleum and Natural Gas
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 - Coal Conversion
 - Hydrogen as a Fuel
 - Other Energy Alternatives

Hot lava flowing into the ocean in Hawaii Volcanoes National Park creates clouds of steam.

Just as energy is important to our society on a macroscopic scale, it is critically important to each living organism on a microscopic scale. The living cell is a miniature chemical factory powered by energy from chemical reactions. The process of cellular respiration extracts the energy stored in sugars and other nutrients to drive the various tasks of the cell. Although the extraction process is more complex and more subtle, the energy obtained from “fuel” molecules by the cell is the same as would be obtained from burning the fuel to power an internal combustion engine.

Whether it is an engine or a cell that is converting energy from one form to another, the processes are all governed by the same principles, which we will begin to explore in this chapter. Additional aspects of energy transformation will be covered in Chapter 16.

6.1 The Nature of Energy

One interesting definition of energy is that which is needed to oppose natural attractions (for example, gravity and electrostatic attractions).

The total energy content of the universe is constant.

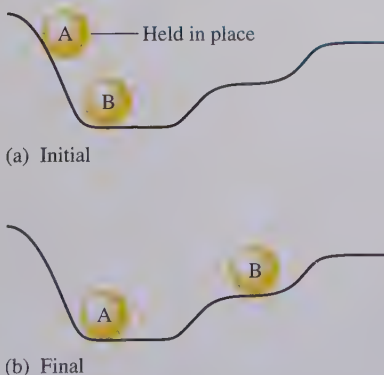


FIGURE 6.1

(a) In the initial positions, ball A has a higher potential energy than ball B. (b) After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.

Although the concept of energy is quite familiar, energy itself is rather difficult to define precisely. We will define **energy** as the *capacity to do work or to produce heat*. In this chapter we will concentrate specifically on the heat transfer that accompanies chemical processes.

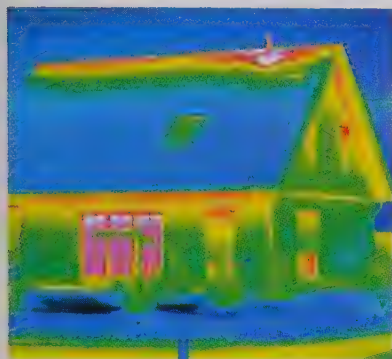
One of the most important characteristics of energy is that it is conserved. The **law of conservation of energy** states that *energy can be converted from one form to another but can be neither created nor destroyed*. That is, the energy of the universe is constant. Energy can be classified as either potential or kinetic energy. **Potential energy** is energy due to position or composition. For example, water behind a dam has potential energy that can be converted to work when the water flows down through turbines, thereby creating electricity. Attractive and repulsive forces also lead to potential energy. The energy released when gasoline is burned results from differences in attractive forces between the nuclei and electrons in the reactants and products. The **kinetic energy** of an object is energy due to the motion of the object and depends on the mass of the object m and its velocity v : $KE = \frac{1}{2}mv^2$.

Energy can be converted from one form to another. For example, consider the two balls in Fig. 6.1(a). Ball A, because of its higher position initially, has more potential energy than ball B. When A is released, it moves down the hill and strikes B. Eventually, the arrangement shown in Fig. 6.1(b) is achieved. What has happened in going from the initial to the final arrangement? The potential energy of A has decreased, but since energy is conserved, all the energy lost by A must be accounted for. How is this energy distributed?

Initially, the potential energy of A is changed to kinetic energy as the ball rolls down the hill. Part of this kinetic energy is then transferred to B, causing it to be raised to a higher final position. Thus the potential energy of B has been increased. However, since the final position of B is lower than the original position of A, some of the energy is still unaccounted for. Both balls in their final positions are at rest, so the missing energy cannot be due to their motions. What has happened to the remaining energy?

The answer lies in the interaction between the hill's surface and the ball. As ball A rolls down the hill, some of its kinetic energy is transferred to the surface of the hill as heat. This transfer of energy is called *frictional heating*. The temperature of the hill increases very slightly as the ball rolls down.

Heat involves a transfer of energy.



This infrared photo of a house shows where energy leaks occur. The more red the color, the more energy (heat) is leaving the house.

Energy is a state function; work and heat are not.

Before we proceed further, it is important to recognize that heat and temperature are decidedly different. As we saw in Chapter 5, *temperature* is a property that reflects the random motions of the particles in a particular substance. **Heat**, on the other hand, involves the *transfer* of energy between two objects due to a temperature difference. Heat is not a substance contained by an object, although we often talk of heat as if this were true.

Note that in going from the initial to the final arrangements in Fig. 6.1, ball B gains potential energy because work was done by ball A on B. **Work** is defined as force acting over a distance. Work is required to raise B from its original position to its final one. Part of the original energy stored as potential energy in A has been transferred through work to B, thereby increasing B's potential energy. Thus there are two ways to transfer energy: through work and through heat.

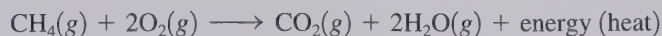
In rolling to the bottom of the hill shown in Fig. 6.1, ball A will always lose the same amount of potential energy. However, the way that this energy transfer is divided between work and heat depends on the specific conditions—the **pathway**. For example, the surface of the hill might be so rough that the energy of A is expended completely through frictional heating; A is moving so slowly when it hits B that it cannot move B to the next level. In this case, no work is done. Regardless of the condition of the hill's surface, the *total energy* transferred will be constant. However, the amounts of heat and work will differ. Energy change is independent of the pathway; however, work and heat are both dependent on the pathway.

This brings us to a very important concept: the **state function** or **state property**. A state function refers to a property of the system that depends only on its *present state*. A state function (property) does not depend in any way on the system's past (or future). In other words, the value of a state function does not depend on how the system arrived at the present state; it depends only on the characteristics of the present state. This leads to a very important characteristic of a state function: A change in this function (property) in going from one state to another state is independent of the particular pathway taken between the two states.

Of the functions considered in our present example, energy is a state function, but work and heat are not state functions.

Chemical Energy

The ideas we have just illustrated using mechanical examples also apply to chemical systems. The combustion of methane, for example, is used to heat many homes in the United States:



To discuss this reaction, we divide the universe into two parts: the system and the surroundings. The **system** is the part of the universe on which we wish to focus attention; the **surroundings** include everything else in the universe. In this case we define the system as the reactants and products of the reaction. The surroundings consist of the reaction container (a furnace, for example), the room, and anything else other than the reactants and products.

When a reaction results in the evolution of heat, it is said to be **exothermic** (*exo-* is a prefix meaning “out of”); that is, energy flows *out of the system*. For example, in the combustion of methane, energy flows out of the system as heat. Reactions that absorb energy from the surroundings are said to be **endothermic**.

When the heat flow is *into a system*, the process is endothermic. For example, the formation of nitric oxide from nitrogen and oxygen is endothermic:



Where does the energy, released as heat, come from in an exothermic reaction? The answer lies in the difference in potential energies between the products and the reactants. Which has lower potential energy, the reactants or the products? We know that total energy is conserved and that energy flows from the system into the surroundings in an exothermic reaction. This means that *the energy gained by the surroundings must be equal to the energy lost by the system*. In the combustion of methane, the energy content of the system decreases, which means that 1 mole of CO_2 and 2 moles of H_2O molecules (the products) possess less potential energy than do 1 mole of CH_4 and 2 moles of O_2 molecules (the reactants). The heat flow into the surroundings results from a lowering of the potential energy of the reaction system. This always holds true. *In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.*

The energy diagram for the combustion of methane is shown in Fig. 6.2, where $\Delta(\text{PE})$ represents the *change* in potential energy stored in the bonds of the products as compared with the bonds of the reactants. In other words, this quantity represents the difference between the energy required to break the bonds in the reactants and the energy released when the bonds in the products are formed. In an exothermic process, the bonds in the products are stronger (on average) than those of the reactants. That is, more energy is released by forming the new bonds in the products than is consumed to break the bonds in the reactants. The net result is that the quantity of energy $\Delta(\text{PE})$ is transferred to the surroundings through heat.

For an endothermic reaction, the situation is reversed, as shown in Fig. 6.3. Energy that flows into the system as heat is used to increase the potential energy of the system. In this case the products have higher potential energy (weaker bonds on average) than the reactants.

The study of energy and its interconversions is called **thermodynamics**. The law of conservation of energy is often called the **first law of thermodynamics** and is stated as follows: *The energy of the universe is constant.*

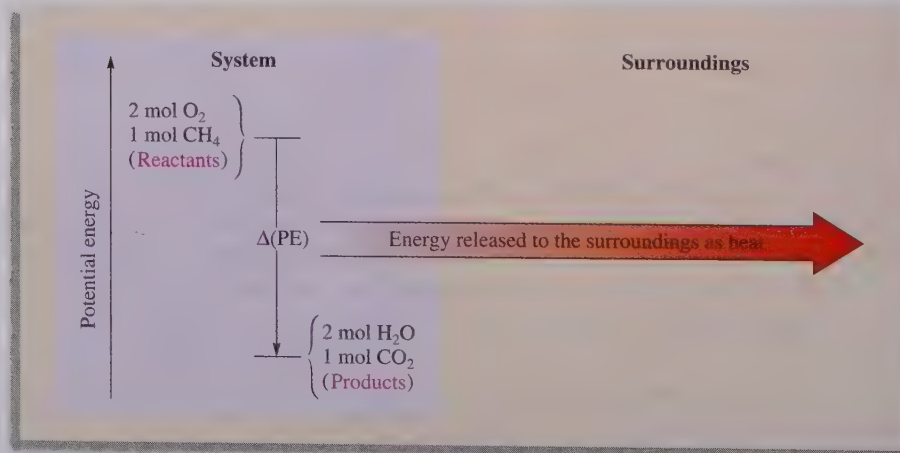
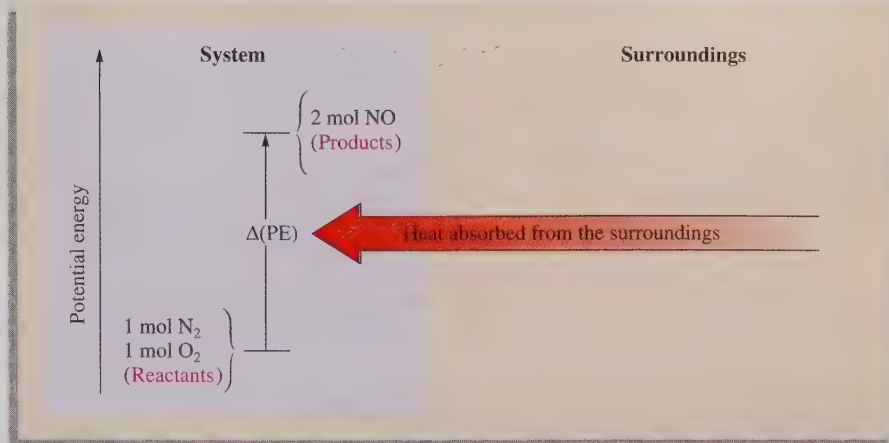


FIGURE 6.2

The combustion of methane releases the quantity of energy $\Delta(\text{PE})$ to the surroundings via heat flow. This is an exothermic process.

FIGURE 6.3

The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat [equal in magnitude to $\Delta(\text{PE})$] flows into the system from the surroundings.

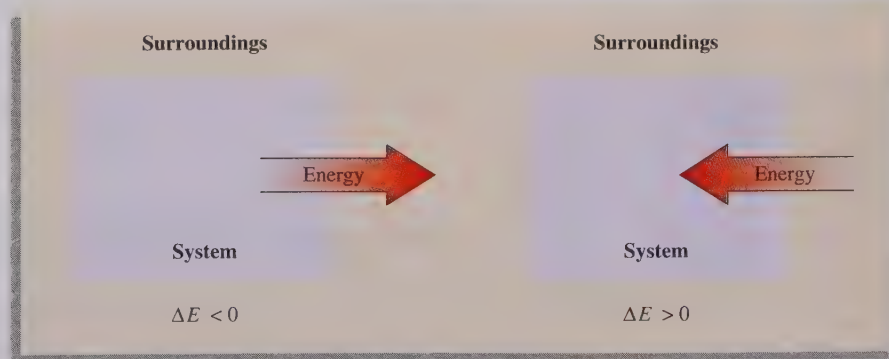


The **internal energy** E of a system can be defined most precisely as the sum of the kinetic and potential energies of all the “particles” in the system. The internal energy of a system can be changed by a flow of work, heat, or both. That is,

$$\Delta E = q + w$$

where ΔE represents the change in the system’s internal energy, q represents heat, and w represents work.

Thermodynamic quantities always consist of two parts: a *number*, giving the magnitude of the change, and a *sign*, indicating the direction of the flow. The *sign* reflects the system’s point of view. For example, if a quantity of energy flows *into* the system via heat (an endothermic process), q is equal to $+x$, where the *positive* sign indicates that the *system’s energy is increasing*. On the other hand, when energy flows *out of* the system via heat (an exothermic process), q is equal to $-x$, where the *negative* sign indicates that the *system’s energy is decreasing*.



In this text the same conventions also apply to the flow of work. If the system does work on the surroundings (energy flows out of the system), w is negative. If the surroundings do work on the system (energy flows into the system), w is positive.

The convention in this text is to take the system's point of view; $q = -x$ denotes an exothermic process, and $q = +x$ denotes an endothermic one.

SAMPLE EXERCISE 6.1

The joule (J) is the fundamental SI unit for energy:

$$\text{J} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

One kilojoule (kJ) = 10^3 J.

We define work from the system's point of view to be consistent for all thermodynamic quantities. That is, in this convention the signs of both q and w reflect what happens to the system; thus we use $\Delta E = q + w$.

In this text we *always* take the system's point of view. This convention is not followed in every area of science. For example, engineers are in the business of designing machines to do work, that is, to make the system (the machine) transfer energy to its surroundings through work. Consequently, engineers define work from the surroundings' point of view. In their convention, work that flows out of the system is treated as positive because the energy of the surroundings has increased. The first law of thermodynamics is then written $\Delta E = q - w'$, where w' signifies work from the surroundings' point of view.

Internal Energy

Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

SOLUTION

We use the equation

$$\Delta E = q + w$$

where $q = +15.6$ kJ, since the process is endothermic, and $w = +1.4$ kJ, since work is done on the system. Thus

$$\Delta E = 15.6 \text{ kJ} + 1.4 \text{ kJ} = 17.0 \text{ kJ}$$

The system has gained 17.0 kJ of energy.

See Exercises 6.21 through 6.24.

A common type of work associated with chemical processes is work done by a gas (through *expansion*) or work done to a gas (through *compression*). For example, in an automobile engine, the heat from the combustion of the gasoline expands the gases in the cylinder to push back the piston, and this motion is then translated into the motion of the car.

Suppose we have a gas confined to a cylindrical container with a movable piston as shown in Fig. 6.4, where F is the force acting on a piston of area A . Since pressure is defined as force per unit area, the pressure of the gas is

$$P = \frac{F}{A}$$

Work is defined as force applied over a distance, so if the piston moves a distance Δh , as shown in Fig. 6.4, then the work done is

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

Since $P = F/A$ or $F = P \times A$, then

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

Since the volume of a cylinder equals the area of the piston times the height of the cylinder (Fig. 6.4), the change in volume ΔV resulting from the piston moving a distance Δh is

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

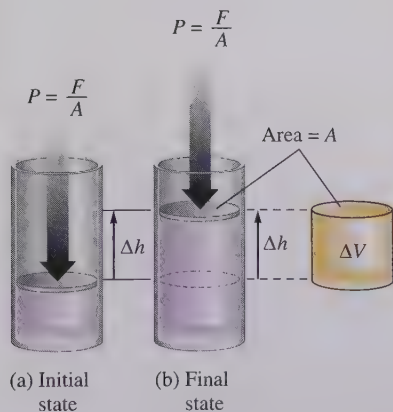


FIGURE 6.4

(a) The piston, moving a distance Δh against a pressure P , does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by $\Delta h \times A = \Delta V$.

Substituting $\Delta V = A \times \Delta h$ into the expression for work gives

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

This gives us the *magnitude* (size) of the work required to expand a gas ΔV against a pressure P .

What about the sign of the work? The gas (the system) is expanding, moving the piston against the pressure. Thus the system is doing work on the surroundings, so from the system's point of view the sign of the work should be negative.

For an *expanding* gas, ΔV is a positive quantity because the volume is increasing. Thus ΔV and w must have opposite signs, which leads to the equation

$$w = -P\Delta V$$

Note that for a gas expanding against an external pressure P , w is a negative quantity as required, since work flows out of the system. When a gas is *compressed*, ΔV is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system).

w and $P\Delta V$ have opposite signs because when the gas expands (ΔV is positive), work flows into the surroundings (w is negative).

SAMPLE EXERCISE 6.2

PV Work

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.

SOLUTION

For a gas at constant pressure,

$$w = -P\Delta V$$

In this case $P = 15$ atm and $\Delta V = 64 - 46 = 18$ L. Hence

$$w = -15 \text{ atm} \times 18 \text{ L} = -270 \text{ L} \cdot \text{atm}$$

Note that since the gas expands, it does work on its surroundings. Energy flows out of the gas, so w is a negative quantity.

See Exercises 6.25 and 6.26.

For an ideal gas, work can occur only when its volume changes. Thus, if a gas is heated at constant volume, the pressure increases but no work occurs.

In dealing with “PV work,” keep in mind that the P in $P\Delta V$ always refers to the external pressure—the pressure that causes a compression or that resists an expansion.

SAMPLE EXERCISE 6.3

Internal Energy, Heat, and Work

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by the addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process. (To convert between L · atm and J, use $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

SOLUTION

To calculate ΔE , we use the equation

$$\Delta E = q + w$$



A propane burner is used to heat the air in a hot air balloon.

Since the problem states that $1.3 \times 10^8 \text{ J}$ of energy is *added* as heat,

$$q = +1.3 \times 10^8 \text{ J}$$

The work done can be calculated from the expression

$$w = -P\Delta V$$

In this case $P = 1.0 \text{ atm}$ and

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}} \\ &= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L} = 5.0 \times 10^5 \text{ L}\end{aligned}$$

Thus

$$w = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L} \cdot \text{atm}$$

Note that the negative sign for w makes sense, since the gas is expanding and thus doing work on the surroundings.

To calculate ΔE , we must sum q and w . However, since q is given in units of J and w is given in units of $\text{L} \cdot \text{atm}$, we must change the work to units of joules:

$$w = -5.0 \times 10^5 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} = -5.1 \times 10^7 \text{ J}$$

Then

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

Since more energy is added through heating than the gas expends doing work, there is a net increase in the internal energy of the gas in the balloon. Hence ΔE is positive.

See Exercises 6.27 and 6.28.

6.2 Enthalpy and Calorimetry

Enthalpy

So far we have discussed the internal energy of a system. A less familiar property of a system is its **enthalpy**, H , which is defined as

$$H = E + PV$$

where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system.

Since internal energy, pressure, and volume are all state functions, *enthalpy is also a state function*. But what exactly is enthalpy? To help answer this question, consider a process carried out at constant pressure and where the only work allowed is pressure–volume work ($w = -P\Delta V$). Under these conditions, the expression

$$\Delta E = q_p + w$$

becomes

$$\Delta E = q_p - P\Delta V$$

or

Enthalpy is a state function. A change in enthalpy does not depend on the pathway between two states.

Recall from the previous section that w and $P\Delta V$ have opposite signs:

$$w = -P\Delta V$$

$$q_P = \Delta E + P\Delta V$$

where q_P is the heat at constant pressure.

We will now relate q_P to a change in enthalpy. The definition of enthalpy is $H = E + PV$. Therefore, we can say

$$\text{Change in } H = (\text{change in } E) + (\text{change in } PV)$$

or

$$\Delta H = \Delta E + \Delta(PV)$$

Since P is constant, the change in PV is due only to a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

$$\Delta H = \Delta E + P\Delta V$$

This expression is identical to the one we obtained for q_P :

$$q_P = \Delta E + P\Delta V$$

Thus, for a process carried out at constant pressure and where the only work allowed is that from a volume change, we have

$$\Delta H = q_P$$

$\Delta H = q$ only at constant pressure.

The change in enthalpy of a system has no easily interpreted meaning except at constant pressure, where $\Delta H = \text{heat}$.

At constant pressure, exothermic means ΔH is negative; endothermic means ΔH is positive.

At constant pressure (where only PV work is allowed), the change in enthalpy ΔH of the system is equal to the energy flow as heat. This means that for a reaction studied at constant pressure, the flow of heat is a measure of the change in enthalpy for the system. For this reason, the terms *heat of reaction* and *change in enthalpy* are used interchangeably for reactions studied at constant pressure.

For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

In a case in which the products of a reaction have a greater enthalpy than the reactants, ΔH will be positive. Thus heat will be absorbed by the system, and the reaction is endothermic. On the other hand, if the enthalpy of the products is less than that of the reactants, ΔH will be negative. In this case the overall decrease in enthalpy is achieved by the generation of heat, and the reaction is exothermic.

SAMPLE EXERCISE 6.4

Enthalpy

When 1 mole of methane (CH_4) is burned at constant pressure, 890 kJ of energy is released as heat. Calculate ΔH for a process in which a 5.8-g sample of methane is burned at constant pressure.

SOLUTION

At constant pressure, 890 kJ of energy per mole of CH_4 is produced as heat:

$$q_P = \Delta H = -890 \text{ kJ/mol CH}_4$$

Note that the minus sign indicates an exothermic process. In this case, a 5.8-g sample of CH_4 (molar mass = 16.0 g/mol) is burned. Since this amount is smaller than

1 mole, less than 890 kJ will be released as heat. The actual value can be calculated as follows:

$$5.8 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} = 0.36 \text{ mol CH}_4$$

and

$$0.36 \text{ mol CH}_4 \times \frac{-890 \text{ kJ}}{\text{mol CH}_4} = -320 \text{ kJ}$$

Thus, when a 5.8-g sample of CH_4 is burned at constant pressure,

$$\Delta H = \text{heat flow} = -320 \text{ kJ}$$

See Exercises 6.33 through 6.36.

Calorimetry

The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimeter**. **Calorimetry**, the science of measuring heat, is based on observing the temperature change when a body absorbs or discharges energy as heat. Substances respond differently to being heated. One substance might require a great deal of heat energy to raise its temperature by one degree, whereas another will exhibit the same temperature change after absorbing relatively little heat. The **heat capacity** C of a substance, which is a measure of this property, is defined as

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

Specific heat capacity: the energy required to raise the temperature of one gram of a substance by one degree Celsius.

Molar heat capacity: the energy required to raise the temperature of one mole of a substance by one degree Celsius.

When an element or a compound is heated, the energy required will depend on the amount of the substance present (for example, it takes twice as much energy to raise the temperature of two grams of water by one degree than it takes to raise the temperature of one gram of water by one degree). Thus, in defining the heat capacity of a substance, the amount of substance must be specified. If the heat capacity is given *per gram* of substance, it is called the **specific heat capacity**, and its units are $\text{J}/^\circ\text{C} \cdot \text{g}$ or $\text{J}/\text{K} \cdot \text{g}$. If the heat capacity is given *per mole* of the substance, it is called the **molar heat capacity**, and it has the units $\text{J}/^\circ\text{C} \cdot \text{mol}$ or $\text{J}/\text{K} \cdot \text{mol}$. The specific heat capacities of some common substances are given in Table 6.1. Note from this table that the heat capacities of metals are very different from that of water. It takes much less energy to change the temperature of a gram of a metal by 1°C than for a gram of water.

Although the calorimeters used for highly accurate work are precision instruments, a very simple calorimeter can be used to examine the fundamentals of calorimetry. All we need are two nested Styrofoam cups with a cover through which a stirrer and thermometer can be inserted, as shown in Fig. 6.5. This device is called a “coffee-cup calorimeter.” The outer cup is used to provide extra insulation. The inner cup holds the solution in which the reaction occurs.

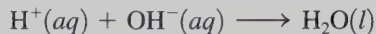
The measurement of heat using a simple calorimeter such as that shown in Fig. 6.5 is an example of **constant-pressure calorimetry**, since the pressure (atmospheric pressure) remains constant during the process. Constant-pressure calorimetry is used in determining the changes in enthalpy (heats of reactions) for

TABLE 6.1
The Specific Heat Capacities
of Some Common
Substances

Substance	Specific Heat Capacity ($\text{J}/^\circ\text{C} \cdot \text{g}$)
$\text{H}_2\text{O}(l)$	4.18
$\text{H}_2\text{O}(s)$	2.03
$\text{Al}(s)$	0.89
$\text{Fe}(s)$	0.45
$\text{Hg}(l)$	0.14
$\text{C}(s)$	0.71

reactions occurring in solution. Recall that under these conditions, the change in enthalpy equals the heat.

For example, suppose we mix 50.0 mL of 1.0 M HCl at 25.0°C with 50.0 mL of 1.0 M NaOH also at 25°C in a calorimeter. After the reactants are mixed by stirring, the temperature is observed to increase to 31.9°C. As we saw in Section 4.8, the net ionic equation for this reaction is



When these reactants (each originally at the same temperature) are mixed, the temperature of the mixed solution is observed to increase. Therefore, the chemical reaction must be releasing energy as heat. This released energy increases the random motions of the solution components, which in turn increases the temperature. The quantity of energy released can be determined from the temperature increase, the mass of solution, and the specific heat capacity of the solution. For an approximate result, we will assume that the calorimeter does not absorb or leak any heat and that the solution can be treated as if it were pure water with a density of 1.0 g/mL.

We also need to know the heat required to raise the temperature of a given amount of water by 1°C. Table 6.1 lists the specific heat capacity of water as 4.18 J/°C · g. This means that 4.18 J of energy is required to raise the temperature of 1 gram of water by 1°C.

From these assumptions and definitions, we can calculate the heat (change in enthalpy) for the neutralization reaction:

Energy released by the reaction

= energy absorbed by the solution

= specific heat capacity × mass of solution × increase in temperature

= $s \times m \times \Delta T$

In this case the increase in temperature (ΔT) = 31.9°C – 25.0°C = 6.9°C, and the mass of solution (m) = 100.0 mL × 1.0 g/mL = 1.0×10^2 g. Thus

$$\begin{aligned} \text{Energy released} &= s \times m \times \Delta T \\ &= \left(4.18 \frac{\text{J}}{^\circ\text{C} \cdot \text{g}}\right)(1.0 \times 10^2 \text{ g})(6.9^\circ\text{C}) \\ &= 2.9 \times 10^3 \text{ J} \end{aligned}$$

How much energy would have been released if twice these amounts of solutions had been mixed? The answer is that twice as much energy would have been produced. The heat of a reaction is an *extensive property*; it depends directly on the amount of substance, in this case on the amounts of reactants. In contrast, an *intensive property* is not related to the amount of a substance. For example, temperature is an intensive property.

Enthalpies of reaction are often expressed in terms of moles of reacting substances. The number of moles of H^+ ions consumed in the preceding experiment is

$$50.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.0 \text{ mol}}{\text{L}} \text{H}^+ = 5.0 \times 10^{-2} \text{ mol H}^+$$

Thus 2.9×10^3 J heat was released when 5.0×10^{-2} mol H^+ ions reacted, or

$$\frac{2.9 \times 10^3 \text{ J}}{5.0 \times 10^{-2} \text{ mol H}^+} = 5.8 \times 10^4 \text{ J/mol}$$

If two reactants at the same temperature are mixed and the resulting solution gets warmer, this means the reaction taking place is exothermic. An endothermic reaction cools the solution.

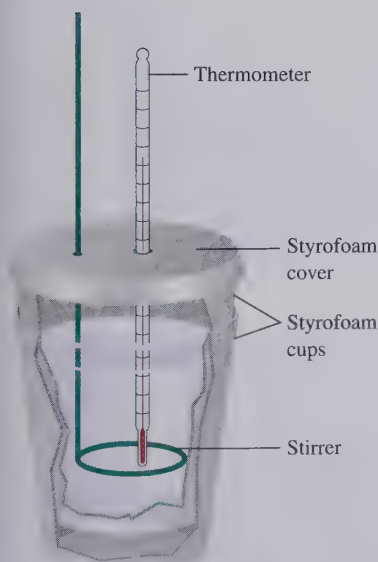


FIGURE 6.5
A coffee-cup calorimeter made of two Styrofoam cups.

CHEMICAL IMPACT

Nature Has Hot Plants

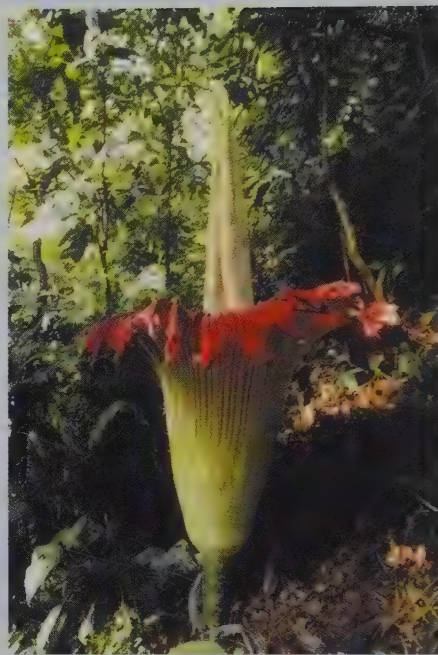
The voodoo lily is a beautiful, seductive—and foul-smelling—plant. The exotic-looking lily features an elaborate reproductive mechanism—a purple spike that can reach nearly 3 feet in length and is cloaked by a hoodlike leaf. But approach to the plant reveals bad news—it smells terrible!

Despite its antisocial odor, this putrid plant has fascinated biologists for many years because of its ability to generate heat. At the peak of its metabolic activity, the plant's blossom can be as much as 15°C above its ambient temperature. To generate this much heat, the metabolic rate of the plant must be close to that of a flying hummingbird!

What's the purpose of this intense heat production? For a plant faced with limited food supplies in the very competitive tropical climate where it grows, heat production seems like a great waste of energy. The answer to this mystery is that the voodoo lily is pollinated mainly by carrion-loving insects. Thus the lily prepares a malodorous mixture of chemicals characteristic of rotting meat, which it then “cooks” off into the surrounding air to attract flesh-feeding beetles and flies. Then, once the insects enter the pollination chamber, the high temperatures there (as high as 110°F) cause the insects to remain very active to better carry out their pollination duties.

The voodoo lily is only one of many such thermogenic (heat-producing) plants. These plants are of special interest to biologists because they provide opportunities to study metabolic reactions that are quite subtle in “normal” plants. For example, recent studies have shown that salicylic acid, the active form of aspirin, is probably very important in producing the metabolic bursts in thermogenic plants.

Besides studying the dramatic heat effects in thermogenic plants, biologists are also interested in calorimetric studies of regular plants. For example, very precise calorimeters have been designed that can be used to study the heat



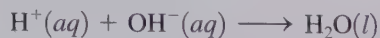
The voodoo lily attracts pollinating insects with its foul odor.

produced, and thus the metabolic activities, of clumps of cells no larger than a bread crumb. Several scientists have suggested that a single calorimetric measurement taking just a few minutes on a tiny plant might be useful in predicting the growth rate of the mature plant throughout its lifetime. If true, this would provide a very efficient method for selecting the plants most likely to thrive as adults.

Because the study of the heat production by plants is an excellent way to learn about plant metabolism, this continues to be a “hot” area of research.

Notice that in this example we mentally keep track of the direction of the energy flow and assign the correct sign at the end of the calculation.

of heat released per 1.0 mol H^+ ions neutralized. Thus the *magnitude* of the enthalpy change per mole for the reaction



is 58 kJ/mol. Since heat is *evolved*, $\Delta H = -58 \text{ kJ/mol}$.

SAMPLE EXERCISE 6.5

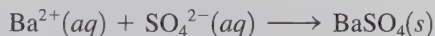
Constant-Pressure Calorimetry

When 1.00 L of 1.00 M $\text{Ba}(\text{NO}_3)_2$ solution at 25.0°C is mixed with 1.00 L of 1.00 M Na_2SO_4 solution at 25°C in a calorimeter, the white solid BaSO_4 forms and the temperature of the mixture increases to 28.1°C . Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solu-

tion is $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$, and that the density of the final solution is 1.0 g/mL , calculate the enthalpy change per mole of BaSO_4 formed.

SOLUTION

The ions present before any reaction occurs are Ba^{2+} , NO_3^- , Na^+ , and SO_4^{2-} . The Na^+ and NO_3^- ions are spectator ions, since NaNO_3 is very soluble in water and will not precipitate under these conditions. The net ionic equation for the reaction is therefore



Since the temperature increases, formation of the solid BaSO_4 must be exothermic; ΔH will be negative.

Heat evolved by reaction

= heat absorbed by solution

= specific heat capacity $\times$ mass of solution $\times$ increase in temperature

Since 1.00 L of each solution is used, the total solution volume is 2.00 L , and

$$\text{Mass of solution} = 2.00 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.0 \text{ g}}{\text{mL}} = 2.0 \times 10^3 \text{ g}$$

$$\text{Temperature increase} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

$$\text{Heat evolved} = (4.18 \text{ J/}^\circ\text{C} \cdot \text{g})(2.0 \times 10^3 \text{ g})(3.1^\circ\text{C}) = 2.6 \times 10^4 \text{ J}$$

Thus

$$q = q_p = \Delta H = -2.6 \times 10^4 \text{ J}$$

Since 1.0 L of $1.0 \text{ M Ba(NO}_3)_2$ contains 1 mol Ba^{2+} ions and 1.0 L of $1.0 \text{ M Na}_2\text{SO}_4$ contains $1.0 \text{ mol SO}_4^{2-}$ ions, 1.0 mol solid BaSO_4 is formed in this experiment. Thus the enthalpy change per mole of BaSO_4 formed is

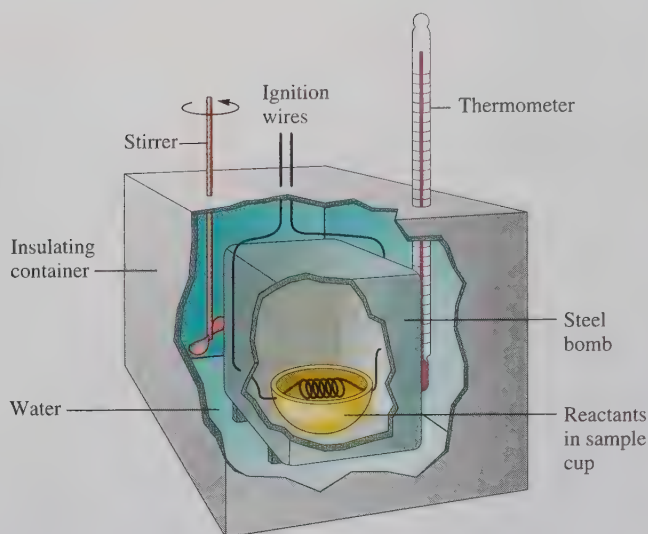
$$\Delta H = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol}$$

See Exercises 6.45 through 6.48.

Calorimetry experiments also can be performed at **constant volume**. For example, when a photographic flashbulb flashes, the bulb becomes very hot, because the reaction of the zirconium or magnesium wire with the oxygen inside the bulb is exothermic. The reaction occurs inside the flashbulb, which is rigid and does not change volume. Under these conditions, no work is done (because the volume must change for pressure–volume work to be performed). To study the energy changes in reactions under conditions of constant volume, a “bomb calorimeter” (Fig. 6.6) is used. Weighed reactants are placed inside a rigid steel container (the “bomb”) and ignited. The energy change is determined by measuring the increase in the temperature of the water and other calorimeter parts. For a constant-volume process, the change in volume ΔV is equal to zero, so work (which is $-P\Delta V$) is also equal to zero. Therefore,

$$\Delta E = q + w = q = q_v \quad (\text{constant volume})$$

Suppose we wish to measure the energy of combustion of octane (C_8H_{18}), a component of gasoline. A 0.5269-g sample of octane is placed in a bomb calorimeter known to have a heat capacity of $11.3 \text{ kJ/}^\circ\text{C}$. This means that 11.3 kJ of energy is

**FIGURE 6.6**

A bomb calorimeter. The reaction is carried out inside a rigid steel “bomb” (photo of actual disassembled “bomb” shown on right), and the heat evolved is absorbed by the surrounding water and other calorimeter parts. The quantity of energy produced by the reaction can be calculated from the temperature increase.

required to raise the temperature of the water and other parts of the calorimeter by 1°C . The octane is ignited in the presence of excess oxygen, and the temperature increase of the calorimeter is 2.25°C . The amount of energy released is calculated as follows:

Energy released by the reaction

$$\begin{aligned} &= \text{temperature increase} \times \text{energy required to change the temperature by } 1^{\circ}\text{C} \\ &= \Delta T \times \text{heat capacity of calorimeter} \\ &= 2.25^{\circ}\text{C} \times 11.3 \text{ kJ}/^{\circ}\text{C} = 25.4 \text{ kJ} \end{aligned}$$

This means that 25.4 kJ of energy was released by the combustion of 0.5269 g octane. The number of moles of octane is

$$0.5269 \text{ g octane} \times \frac{1 \text{ mol octane}}{114.2 \text{ g octane}} = 4.614 \times 10^{-3} \text{ mol octane}$$

Since 25.4 kJ of energy was released for 4.614×10^{-3} mol octane, the energy released per mole is

$$\frac{25.4 \text{ kJ}}{4.614 \times 10^{-3} \text{ mol}} = 5.50 \times 10^3 \text{ kJ/mol}$$

Since the reaction is exothermic, ΔE is negative:

$$\Delta E_{\text{combustion}} = -5.50 \times 10^3 \text{ kJ/mol}$$

Note that since no work is done in this case, ΔE is equal to the heat.

$$\Delta E = q + w = q \quad \text{since } w = 0$$

Thus $q = -5.50 \times 10^3 \text{ kJ/mol}$.

CHEMICAL IMPACT

Firewalking: Magic or Science?

For millennia people have been amazed at the ability of Eastern mystics to walk across beds of glowing coals without any apparent discomfort. Even in the United States, thousands of people have performed feats of firewalking as part of motivational seminars. How is this possible? Do firewalkers have supernatural powers?

Actually, there are good scientific explanations, based on the concepts covered in this chapter, of why firewalking is possible. The first important factor concerns the heat capacity of feet. Because human tissue is mainly composed of water, it has a relatively large specific heat capacity. This means that a large amount of energy must be transferred from the coals to significantly change the temperature of the feet. During the brief contact between feet and coals, there is relatively little time for energy flow so the feet do not reach a high enough temperature to cause damage.

Second, although the surface of the coals has a very high temperature, the red hot layer is very thin. Therefore, the quantity of energy available to heat the feet is smaller than might be expected. This factor points to the difference between temperature and heat. Temperature reflects the *intensity* of the random kinetic energy in a given sample of matter. The amount of energy available for heat flow, on the other hand, depends on the quantity of matter at a given temperature—10 grams of matter at a given temperature

contains 10 times as much thermal energy as 1 gram of the same matter. This is why the tiny spark from a sparkler does not hurt when it hits your hand. The spark has a very high temperature but has so little mass that no significant energy transfer occurs to your hand. This same argument applies to the very thin hot layer on the coals.

Thus, although firewalking is an impressive feat, there are several sound scientific reasons why it is possible (with the proper training and a properly prepared bed of coals).



A group of firewalkers in Japan.

SAMPLE EXERCISE 6.6

Hydrogen's potential as a fuel is discussed in Section 6.6.

Constant-Volume Calorimetry

It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of $11.3 \text{ kJ/}^\circ\text{C}$. When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3°C . When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3°C . Calculate the energy of combustion (per gram) for hydrogen and methane.

The direction of energy flow is indicated by words in this example. Using signs to designate the direction of energy flow:

$$\Delta E_{\text{combustion}} = -55 \text{ kJ/g}$$

for methane and

$$\Delta E_{\text{combustion}} = -141 \text{ kJ/g}$$

for hydrogen.

SOLUTION

We calculate the energy of combustion for methane using the heat capacity of the calorimeter (11.3 kJ/°C) and the observed temperature increase of 7.3°C:

$$\begin{aligned} \text{Energy released in the combustion of 1.5 g CH}_4 &= (11.3 \text{ kJ/}^\circ\text{C})(7.3^\circ\text{C}) \\ &= 83 \text{ kJ} \end{aligned}$$

$$\text{Energy released in the combustion of 1 g CH}_4 = \frac{83 \text{ kJ}}{1.5 \text{ g}} = 55 \text{ kJ/g}$$

Similarly, for hydrogen

$$\begin{aligned} \text{Energy released in the combustion of 1.15 g H}_2 &= (11.3 \text{ kJ/}^\circ\text{C})(14.3^\circ\text{C}) \\ &= 162 \text{ kJ} \end{aligned}$$

$$\text{Energy released in the combustion of 1 g H}_2 = \frac{162 \text{ kJ}}{1.15 \text{ g}} = 141 \text{ kJ/g}$$

The energy released in the combustion of 1 g hydrogen is approximately 2.5 times that for 1 g methane, indicating that hydrogen gas is a potentially useful fuel.

See Exercises 6.49 and 6.50.

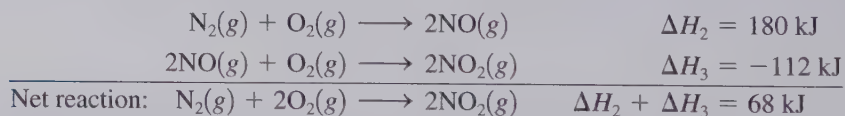
6.3 Hess's Law

ΔH is not dependent on the reaction pathway.

Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. This means that *in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps*. This principle is known as **Hess's law** and can be illustrated by examining the oxidation of nitrogen to produce nitrogen dioxide. The overall reaction can be written in one step, where the enthalpy change is represented by ΔH_1 .



This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3 :



Note that the sum of the two steps gives the net, or overall, reaction and that

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \text{ kJ}$$

The principle of Hess's law is shown schematically in Fig. 6.7.

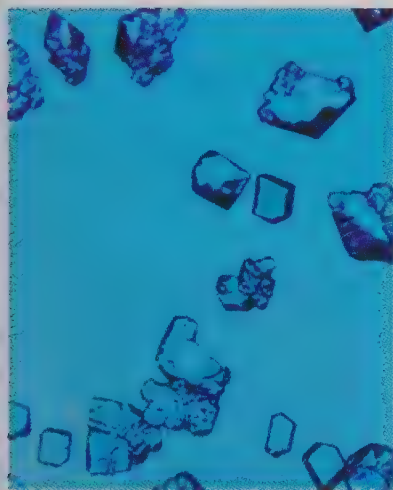
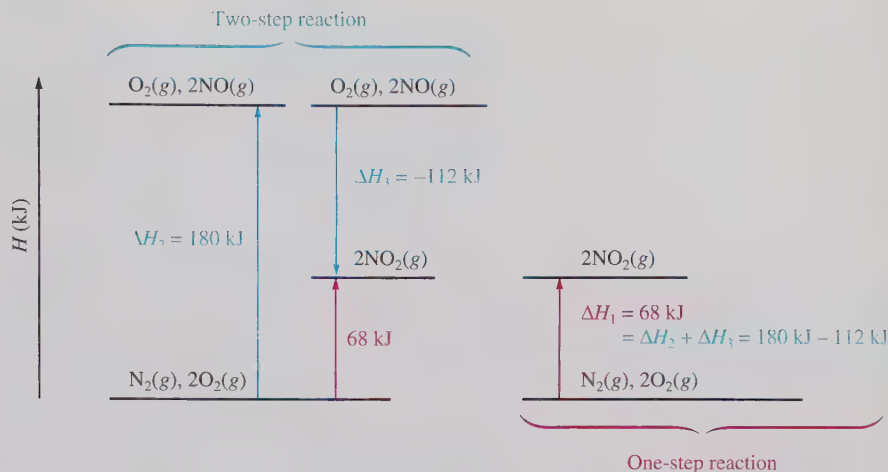
Characteristics of Enthalpy Changes

Reversing the direction of a reaction changes the sign of ΔH .

To use Hess's law to compute enthalpy changes for reactions, it is important to understand two characteristics of ΔH for a reaction:

FIGURE 6.7

The principle of Hess's law. The same change in enthalpy occurs when nitrogen and oxygen react to form nitrogen dioxide, regardless of whether the reaction occurs in one (red) or two (blue) steps.



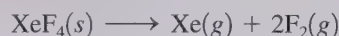
Crystals of xenon tetrafluoride, the first reported binary compound containing a noble gas element.

1. If a reaction is reversed, the sign of ΔH is also reversed.
2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Both these rules follow in a straightforward way from the properties of enthalpy changes. The first rule can be explained by recalling that the *sign* of ΔH indicates the *direction* of the heat flow at constant pressure. If the direction of the reaction is reversed, the direction of the heat flow also will be reversed. To see this, consider the preparation of xenon tetrafluoride, which was the first binary compound made from a noble gas:

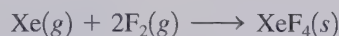


This reaction is exothermic, and 251 kJ of energy flows into the surroundings as heat. On the other hand, if the colorless XeF_4 crystals are decomposed into the elements, according to the equation

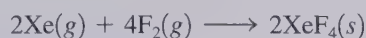


the opposite energy flow occurs because 251 kJ of energy must be added to the system to produce this endothermic reaction. Thus, for this reaction, $\Delta H = +251 \text{ kJ}$.

The second rule comes from the fact that ΔH is an extensive property, depending on the amount of substances reacting. For example, since 251 kJ of energy is evolved for the reaction



then for a preparation involving twice the quantities of reactants and products, or



twice as much heat would be evolved:

$$\Delta H = 2(-251 \text{ kJ}) = -502 \text{ kJ}$$

SAMPLE EXERCISE 6.7

Hess's Law I

Two forms of carbon are *graphite*, the soft, black, slippery material used in “lead” pencils and as a lubricant for locks, and *diamond*, the brilliant, hard gemstone. Using the enthalpies of combustion for graphite (-394 kJ/mol) and diamond (-396 kJ/mol), calculate ΔH for the conversion of graphite to diamond:

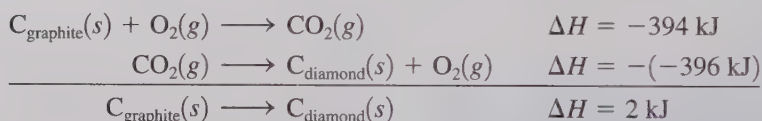


SOLUTION

The combustion reactions are

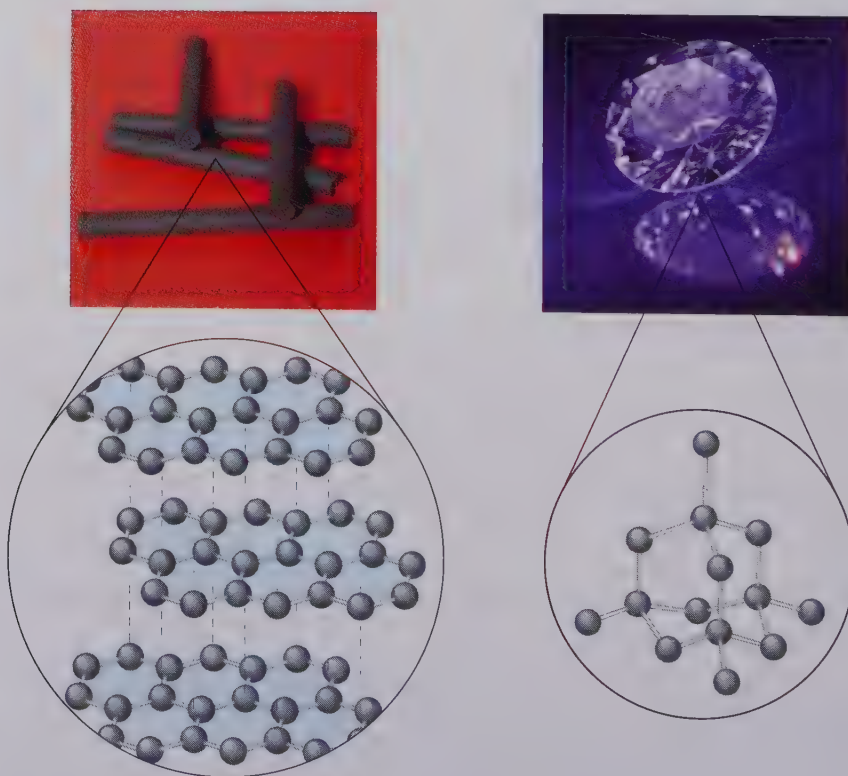


Note that if we reverse the second reaction (which means we must change the sign of ΔH) and sum the two reactions, we obtain the desired reaction:



Thus 2 kJ of energy is required to change 1 mol graphite to diamond. This process is endothermic.

See Exercises 6.51 and 6.52.

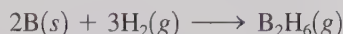


(left) graphite; (right) diamond.

SAMPLE EXERCISE 6.8

Hess's Law II

Diborane (B_2H_6) is a highly reactive boron hydride, which was once considered as a possible rocket fuel for the U.S. space program. Calculate ΔH for the synthesis of diborane from its elements, according to the equation



using the following data:

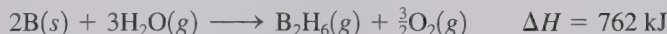
Reaction	ΔH
(a) $2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s)$	-1273 kJ
(b) $\text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g)$	-2035 kJ
(c) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$	-286 kJ
(d) $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44 kJ

SOLUTION

To obtain ΔH for the required reaction, we must somehow combine equations (a), (b), (c), and (d) to produce that reaction and add the corresponding ΔH values. This can best be done by focusing on the reactants and products of the required reaction. The reactants are $\text{B}(s)$ and $\text{H}_2(g)$, and the product is $\text{B}_2\text{H}_6(g)$. How can we obtain the correct equation? Reaction (a) has $\text{B}(s)$ as a reactant, as needed in the required equation. Thus reaction (a) will be used as it is. Reaction (b) has $\text{B}_2\text{H}_6(g)$ as a reactant, but this substance is needed as a product. Thus reaction (b) must be reversed, and the sign of ΔH must be changed accordingly. Up to this point we have

(a)	$2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s)$	$\Delta H = -1273 \text{ kJ}$
-(b)	$\text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + 3\text{O}_2(g)$	$\Delta H = -(-2035 \text{ kJ})$
Sum:	$\text{B}_2\text{O}_3(s) + 2\text{B}(s) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{O}_3(s) + \text{B}_2\text{H}_6(g) + 3\text{O}_2(g)$	$\Delta H = 762 \text{ kJ}$

Deleting the species that occur on both sides gives



We are closer to the required reaction, but we still need to remove $\text{H}_2\text{O}(g)$ and $\text{O}_2(g)$ and introduce $\text{H}_2(g)$ as a reactant. We can do this using reactions (c) and (d). If we multiply reaction (c) and its ΔH value by 3 and add the result to the preceding equation, we have

	$2\text{B}(s) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + \frac{3}{2}\text{O}_2(g)$	$\Delta H = 762 \text{ kJ}$
$3 \times \text{(c)}$	$3[\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)]$	$\Delta H = 3(-286 \text{ kJ})$
Sum:	$2\text{B}(s) + 3\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(l)$	$\Delta H = -96 \text{ kJ}$

We can cancel the $\frac{3}{2}\text{O}_2(g)$ on both sides, but we cannot cancel the H_2O because it is gaseous on one side and liquid on the other. This can be solved by adding reaction (d), multiplied by 3:

	$2\text{B}(s) + 3\text{H}_2(g) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + 3\text{H}_2\text{O}(l)$	$\Delta H = -96 \text{ kJ}$
$3 \times \text{(d)}$	$3[\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)]$	$\Delta H = 3(44 \text{ kJ})$
Sum:	$2\text{B}(s) + 3\text{H}_2(g) + 3\text{H}_2\text{O}(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{B}_2\text{H}_6(g) + 3\text{H}_2\text{O}(l) + 3\text{H}_2\text{O}(g)$	$\Delta H = +36 \text{ kJ}$

This gives the reaction required by the problem:



Thus ΔH for the synthesis of 1 mol diborane from the elements is $+36 \text{ kJ}$.

See Exercises 6.53 through 6.58.

Calculations involving Hess's law typically require that several reactions be manipulated and combined to finally give the reaction of interest. In doing this procedure you should work *backward* from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal. Reverse any reactions as needed to give the required reactants and products, and then multiply reactions to give the correct numbers of reactants and products. This process involves some trial and error, but it can be very systematic if you always allow the final reaction to guide you.

6.4 Standard Enthalpies of Formation

For a reaction studied under conditions of constant pressure, we can obtain the enthalpy change using a calorimeter. However, this process can be very difficult. In fact, in some cases it is impossible, since certain reactions do not lend themselves to such study. An example is the conversion of solid carbon from its graphite form to its diamond form:



The value of ΔH for this process cannot be obtained by direct measurement in a calorimeter because the process is much too slow under normal conditions. However, as we saw in Sample Exercise 6.7, ΔH for this process can be calculated from heats of combustion. This is only one example of how useful it is to be able to *calculate* ΔH values for chemical reactions. We will next show how to do this using standard enthalpies of formation.

The **standard enthalpy of formation** (ΔH_f°) of a compound is defined as the *change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states*.

A *degree symbol* on a thermodynamic function, for example, ΔH° , indicates that the corresponding process has been carried out under standard conditions. The **standard state** for a substance is a precisely defined reference state. Because thermodynamic functions often depend on the concentrations (or pressures) of the substances involved, we must use a common reference state to properly compare the thermodynamic properties of two substances. This is especially important because, for most thermodynamic properties, we can measure only *changes* in the property. For example, we have no method for determining absolute values of enthalpy. We can measure enthalpy changes (ΔH values) only by performing heat-flow experiments.

Conventional Definitions of Standard States

For a Compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For a substance present in a solution, the standard state is a concentration of exactly 1 *M*.

For an Element

- The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25°C. (The standard state for oxygen is $\text{O}_2(g)$ at a pressure of 1 atmosphere; the standard state for sodium is $\text{Na}(s)$; the standard state for mercury is $\text{Hg}(l)$; and so on.)

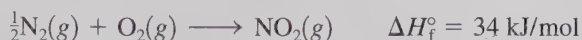
Recently, the International Union of Pure and Applied Chemists (IUPAC) has adopted 1 bar (100,000 Pa) as the standard pressure instead of 1 atm (101,305 Pa). Both standards are now in wide use.

Standard state is *not* the same as the standard temperature and pressure (STP) for a gas (discussed in Section 5.4).



Brown nitrogen dioxide gas.

Several important characteristics of the definition of the enthalpy of formation will become clearer if we again consider the formation of nitrogen dioxide from the elements in their standard states:



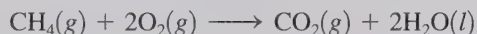
Note that the reaction is written so that both elements are in their standard states, and 1 mole of product is formed. Enthalpies of formation are *always* given per mole of product with the product in its standard state.

The formation reaction for methanol is written as



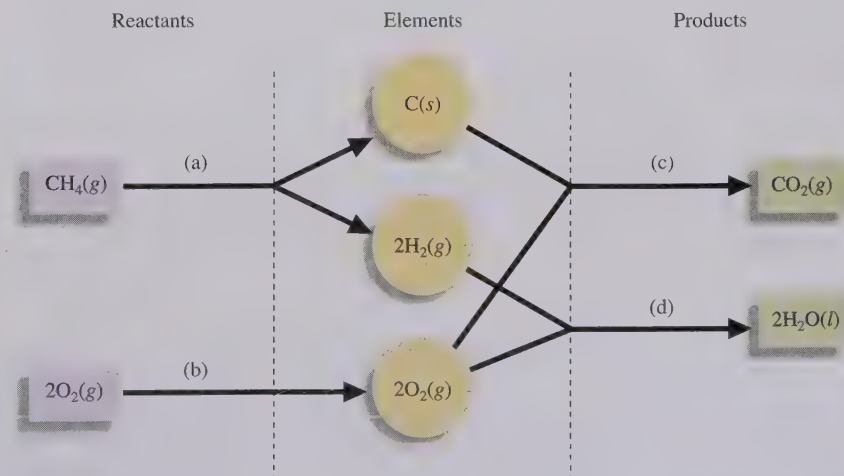
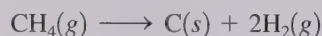
The standard state of carbon is graphite, the standard states for oxygen and hydrogen are the diatomic gases, and the standard state for methanol is the liquid.

The ΔH_f° values for some common substances are shown in Table 6.2. More values are found in Appendix 4. The importance of the tabulated ΔH_f° values is that enthalpies for many reactions can be calculated using these numbers. To see how this is done, we will calculate the standard enthalpy change for the combustion of methane:



Enthalpy is a state function, so we can invoke Hess's law and choose *any* convenient pathway from reactants to products and then sum the enthalpy changes along the chosen pathway. A convenient pathway, shown in Fig. 6.8, involves taking the reactants apart to the respective elements in their standard states in reactions (a) and (b) and then forming the products from these elements in reactions (c) and (d). This general pathway will work for any reaction, since atoms are conserved in a chemical reaction.

Note from Fig. 6.8 that reaction (a), where methane is taken apart into its elements,

**FIGURE 6.8**

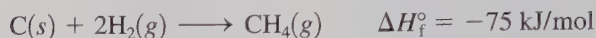
In this pathway for the combustion of methane, the reactants are first taken apart in reactions (a) and (b) to form the constituent elements in their standard states, which are then used to assemble the products in reactions (c) and (d).

TABLE 6.2

Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH_f° (kJ/mol)
NH ₃ (g)	-46
NO ₂ (g)	34
H ₂ O(l)	-286
Al ₂ O ₃ (s)	-1676
Fe ₂ O ₃ (s)	-826
CO ₂ (g)	-394
CH ₃ OH(l)	-239
C ₈ H ₁₈ (l)	-269

is just the reverse of the formation reaction for methane:



Since reversing a reaction means changing the sign of ΔH but keeping the magnitude the same, ΔH for reaction (a) is $-\Delta H_f^\circ$, or 75 kJ. Thus $\Delta H_{(a)}^\circ = 75 \text{ kJ}$.

Next we consider reaction (b). Here oxygen is already an element in its standard state, so no change is needed. Thus $\Delta H_{(b)}^\circ = 0$.

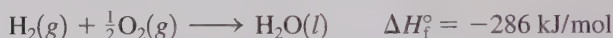
The next steps, reactions (c) and (d), use the elements formed in reactions (a) and (b) to form the products. Note that reaction (c) is simply the formation reaction for carbon dioxide:



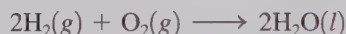
and

$$\Delta H_{(c)}^\circ = \Delta H_f^\circ \text{ for } \text{CO}_2(g) = -394 \text{ kJ}$$

Reaction (d) is the formation reaction for water:



However, since 2 moles of water are required in the balanced equation, we must form 2 moles of water from the elements:



Thus

$$\Delta H_{(d)}^\circ = 2 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l) = 2(-286 \text{ kJ}) = -572 \text{ kJ}$$

We have now completed the pathway from the reactants to the products. The change in enthalpy for the reaction is the sum of the ΔH values (including their signs) for the steps:

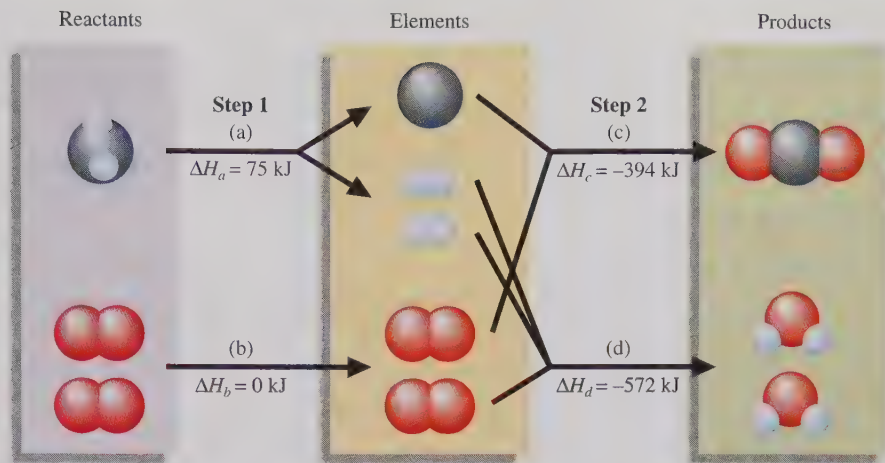
$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= \Delta H_{(a)}^\circ + \Delta H_{(b)}^\circ + \Delta H_{(c)}^\circ + \Delta H_{(d)}^\circ \\ &= [-\Delta H_f^\circ \text{ for } \text{CH}_4(g)] + 0 + [\Delta H_f^\circ \text{ for } \text{CO}_2(g)] + [2 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l)] \\ &= -(-75 \text{ kJ}) + 0 + (-394 \text{ kJ}) + (-572 \text{ kJ}) \\ &= -891 \text{ kJ} \end{aligned}$$

This process is diagrammed in Fig. 6.9. Notice that the reactants are taken apart and converted to elements [not necessary for $\text{O}_2(g)$] that are then used to form products. You can see that this is a very exothermic reaction because very little energy is required to convert the reactants to the respective elements but a great deal of energy is released when these elements form the products. This is why this reaction is so useful for producing heat to warm homes and offices.

Let's examine carefully the pathway we used in this example. First, the reactants were broken down into the elements in their standard states. This process involved reversing the formation reactions and thus switching the signs of the enthalpies of formation. The products were then constructed from these elements. This involved formation reactions and thus enthalpies of formation. We can summarize this entire process as follows: *The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.* Remember to multiply the enthalpies of formation by integers as required by the balanced equation. This statement can be

Subtraction means to reverse the sign and add.

FIGURE 6.9
A schematic diagram of the energy changes for the reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$.



represented symbolically as follows:

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants}) \quad (6.1)$$

where the symbol Σ (sigma) means “to take the sum of the terms,” and n_p and n_r represent the moles of each product or reactant, respectively.

Elements are not included in the calculation because elements require no change in form. We have in effect defined the enthalpy of formation of an element in its standard state as zero, since we have chosen this as our reference point for calculating enthalpy changes in reactions.

Elements in their standard states are not included in enthalpy calculations using ΔH°_f values.

Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

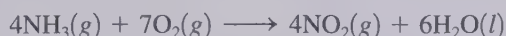
$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is, ΔH°_f for an element in its standard state is zero.

SAMPLE EXERCISE 6.9

Enthalpies from Standard Enthalpies of Formation I

Using the standard enthalpies of formation listed in Table 6.2, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.



SOLUTION

We will use the pathway in which the reactants are broken down into elements in their standard states, which are then used to form the products (see Fig. 6.10).

STEP 1 *Decomposition of $\text{NH}_3(g)$ into elements* (reaction (a) in Fig. 6.10). The first step is to decompose 4 moles of NH_3 into N_2 and H_2 :



The preceding reaction is 4 times the *reverse* of the formation reaction for NH_3 :



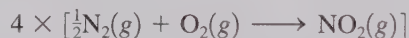
Thus

$$\Delta H_{(a)}^\circ = 4 \text{ mol}[-(-46 \text{ kJ/mol})] = 184 \text{ kJ}$$

STEP 2 *Elemental oxygen* (reaction (b) in Fig. 6.10). Since $\text{O}_2(g)$ is an element in its standard state, $\Delta H_{(b)}^\circ = 0$.

We now have the elements $\text{N}_2(g)$, $\text{H}_2(g)$, and $\text{O}_2(g)$, which can be combined to form the products of the overall reaction.

STEP 3 *Synthesis of $\text{NO}_2(g)$ from elements* (reaction (c) in Fig. 6.10). The overall reaction equation has 4 moles of NO_2 . Thus the required reaction is 4 times the formation reaction for NO_2 :



and

$$\Delta H_{(c)}^\circ = 4 \times \Delta H_f^\circ \text{ for } \text{NO}_2(g)$$

From Table 6.2, ΔH_f° for $\text{NO}_2(g) = 34 \text{ kJ/mol}$ and

$$\Delta H_{(c)}^\circ = 4 \text{ mol} \times 34 \text{ kJ/mol} = 136 \text{ kJ}$$

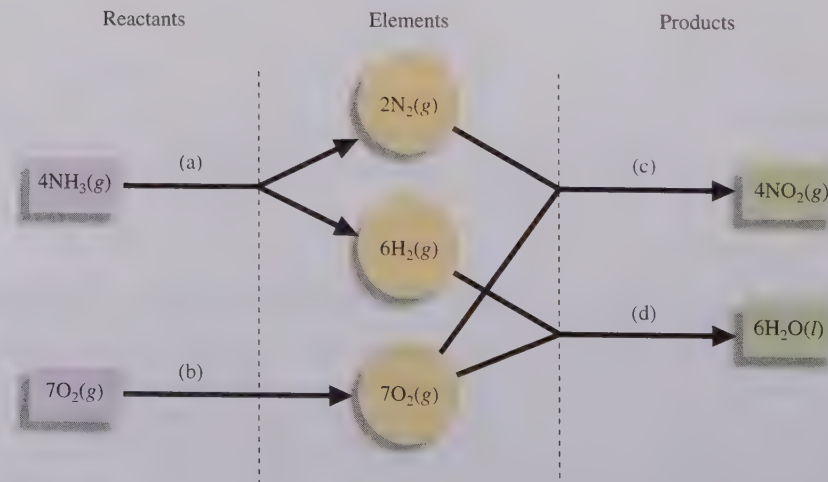
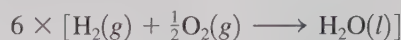


FIGURE 6.10
A pathway for the combustion of ammonia.

STEP 4 *Synthesis of $\text{H}_2\text{O}(l)$ from elements* (reaction (d) in Fig. 6.10). Since the overall equation for the reaction has 6 moles of $\text{H}_2\text{O}(l)$, the required reaction is 6 times the formation reaction for $\text{H}_2\text{O}(l)$:



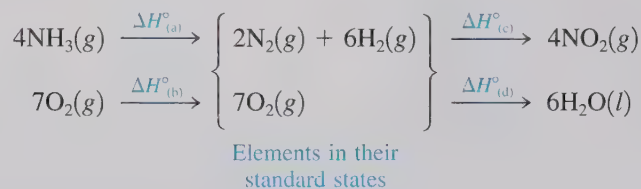
and

$$\Delta H^\circ_{(d)} = 6 \times \Delta H^\circ_f \text{ for } \text{H}_2\text{O}(l)$$

From Table 6.2, ΔH°_f for $\text{H}_2\text{O}(l) = -286 \text{ kJ/mol}$ and

$$\Delta H^\circ_{(d)} = 6 \text{ mol } (-286 \text{ kJ/mol}) = -1716 \text{ kJ}$$

To summarize, we have done the following:



We add the ΔH° values for the steps to get ΔH° for the overall reaction:

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)} \\ &= [4 \times -\Delta H^\circ_f \text{ for } \text{NH}_3(g)] + 0 + [4 \times \Delta H^\circ_f \text{ for } \text{NO}_2(g)] \\ &\quad + [6 \times \Delta H^\circ_f \text{ for } \text{H}_2\text{O}(l)] \\ &= [4 \times \Delta H^\circ_f \text{ for } \text{NO}_2(g)] + [6 \times \Delta H^\circ_f \text{ for } \text{H}_2\text{O}(l)] \\ &\quad - [4 \times \Delta H^\circ_f \text{ for } \text{NH}_3(g)] \\ &= \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants}) \end{aligned}$$

Remember that elemental reactants and products do not need to be included, since ΔH°_f for an element in its standard state is zero. Note that we have again obtained Equation (6.1). The final solution is

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= [4 \times (34 \text{ kJ})] + [6 \times (-286 \text{ kJ})] - [4 \times (-46 \text{ kJ})] \\ &= -1396 \text{ kJ} \end{aligned}$$

See Exercises 6.61 and 6.62.

Now that we have shown the basis for Equation (6.1), we will make direct use of it to calculate ΔH for reactions in succeeding exercises.

SAMPLE EXERCISE 6.10



Visualization: Thermite Reaction

Enthalpies from Standard Enthalpies of Formation II

Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:



The thermite reaction is one of the most energetic chemical reactions known.



This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse.

SOLUTION

We use Equation (6.1):

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

where

$$\Delta H_f^\circ \text{ for } \text{Fe}_2\text{O}_3(s) = -826 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for } \text{Al}_2\text{O}_3(s) = -1676 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for } \text{Al}(s) = \Delta H_f^\circ \text{ for } \text{Fe}(s) = 0$$

Thus

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= \Delta H_f^\circ \text{ for } \text{Al}_2\text{O}_3(s) - \Delta H_f^\circ \text{ for } \text{Fe}_2\text{O}_3(s) \\ &= -1676 \text{ kJ} - (-826 \text{ kJ}) = -850 \text{ kJ} \end{aligned}$$

This reaction is so highly exothermic that the iron produced is initially molten. This process is often used as a lecture demonstration and also has been used in welding massive steel objects such as ships' propellers.

See Exercises 6.65 and 6.66.

SAMPLE EXERCISE 6.11

Enthalpies from Standard Enthalpies of Formation III

Methanol (CH_3OH) is often used as a fuel in high-performance engines in race cars. Using the data in Table 6.2, compare the standard enthalpy of combustion per gram of methanol with that per gram of gasoline. Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane (C_8H_{18}).

SOLUTION

The combustion reaction for methanol is



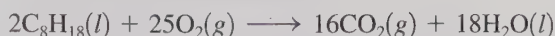
Using the standard enthalpies of formation from Table 6.2 and Equation (6.1), we have

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= 2 \times \Delta H_f^\circ \text{ for } \text{CO}_2(g) + 4 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l) - \\ &\quad 2 \times \Delta H_f^\circ \text{ for } \text{CH}_3\text{OH}(l) \\ &= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ}) \\ &= -1454 \text{ kJ} \end{aligned}$$

Thus 1454 kJ of heat is evolved when 2 moles of methanol burn. The molar mass of methanol is 32.0 g/mol. This means that 1454 kJ of energy is produced when 64.0 g methanol burns. The enthalpy of combustion per gram of methanol is

$$\frac{-1454 \text{ kJ}}{64.0 \text{ g}} = -22.7 \text{ kJ/g}$$

The combustion reaction for octane is



Using the standard enthalpies of information from Table 6.2 and Equation (6.1), we have

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 16 \times \Delta H^\circ_f \text{ for } \text{CO}_2(g) + 18 \times \Delta H^\circ_f \text{ for } \text{H}_2\text{O}(l) - \\ &\quad 2 \times \Delta H^\circ_f \text{ for } \text{C}_8\text{H}_{18}(l) \\ &= 16 \times (-394 \text{ kJ}) + 18 \times (-286 \text{ kJ}) - 2 \times (-269 \text{ kJ}) \\ &= -1.09 \times 10^4 \text{ kJ}\end{aligned}$$

This is the amount of heat evolved when 2 moles of octane burn. Since the molar mass of octane is 114.2 g/mol, the enthalpy of combustion per gram of octane is

$$\frac{-1.09 \times 10^4 \text{ kJ}}{2(114.2 \text{ g})} = -47.8 \text{ kJ/g}$$

The enthalpy of combustion per gram of octane is approximately twice that per gram of methanol. On this basis, gasoline appears to be superior to methanol for use in a racing car, where weight considerations are usually very important. Why then is methanol in fact used in racing cars? The answer is that methanol burns much more smoothly than gasoline in high-performance engines, and this advantage more than compensates for its weight disadvantage.

See Exercise 6.71.

6.5 Present Sources of Energy

Woody plants, coal, petroleum, and natural gas provide a vast resource of energy that originally came from the sun. By the process of photosynthesis, plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted over millions of years to **fossil fuels**. Although the United States currently depends heavily on petroleum for energy, this dependency is a relatively recent phenomenon, as shown in Fig. 6.11. In this section we discuss some sources of energy and their effects on the environment.

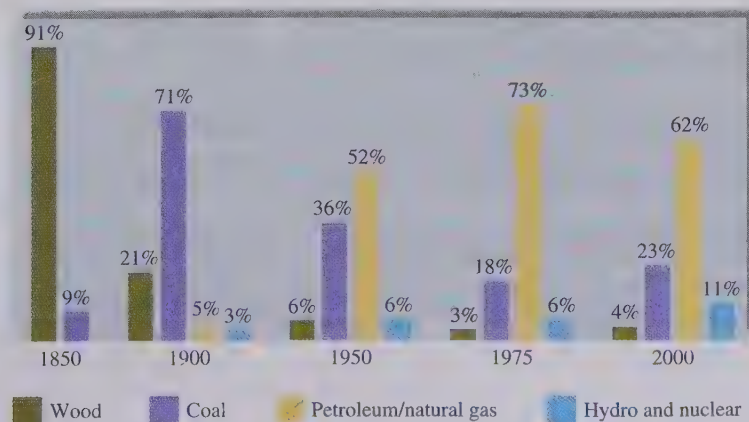


FIGURE 6.11
Energy sources used in the United States.

Petroleum and Natural Gas

Although how they were produced is not completely understood, petroleum and natural gas were most likely formed from the remains of marine organisms that lived approximately 500 million years ago. **Petroleum** is a thick, dark liquid composed mostly of compounds called *hydrocarbons* that contain carbon and hydrogen. (Carbon is unique among elements in the extent to which it can bond to itself to form chains of various lengths.) Table 6.3 gives the formulas and names for several common hydrocarbons. **Natural gas**, usually associated with petroleum deposits, consists mostly of methane, but it also contains significant amounts of ethane, propane, and butane.

The composition of petroleum varies somewhat, but it consists mostly of hydrocarbons having chains that contain from 5 to more than 25 carbons. To be used efficiently, the petroleum must be separated into fractions by boiling. The lighter molecules (having the lowest boiling points) can be boiled off, leaving the heavier ones behind. The commercial uses of various petroleum fractions are shown in Table 6.4.

The petroleum era began when the demand for lamp oil during the Industrial Revolution outstripped the traditional sources: animal fats and whale oil. In response to this increased demand, Edwin Drake drilled the first oil well in 1859 at Titusville, Pennsylvania. The petroleum from this well was refined to produce *kerosene* (fraction C_{10} – C_{18}), which served as an excellent lamp oil. *Gasoline* (fraction C_5 – C_{10}) had limited use and was often discarded. However this situation soon changed. The development of the electric light decreased the need for kerosene, and the advent of the “horseless carriage” with its gasoline-powered engine signaled the birth of the gasoline age.

As gasoline became more important, new ways were sought to increase the yield of gasoline obtained from each barrel of petroleum. William Burton invented a process at Standard Oil of Indiana called *pyrolytic (high-temperature) cracking*. In this process, the heavier molecules of the kerosene fraction are heated to about 700°C , causing them to break (crack) into the smaller molecules of hydrocarbons in the gasoline fraction. As cars became larger, more efficient internal combustion engines were designed. Because of the uneven burning of the gasoline then available, these engines “knocked,” producing unwanted noise and even engine damage. Intensive research to find additives that would promote smoother burning produced tetraethyl lead, $(C_2H_5)_4Pb$, a very effective “antiknock” agent.

The addition of tetraethyl lead to gasoline became a common practice, and by 1960, gasoline contained as much as 3 grams of lead per gallon. As we have discovered so often in recent years, technological advances can produce environmental problems. To prevent air pollution from automobile exhaust, catalytic converters have been added to car exhaust systems. The effectiveness of these converters, however, is destroyed by lead. The use of leaded gasoline also greatly increased the amount of lead in the environment, where it can be ingested by animals and humans. For these reasons, the use of lead in gasoline has

TABLE 6.3
Names and Formulas for
Some Common Hydrocarbons

Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

TABLE 6.4
Uses of the Various
Petroleum Fractions

Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C_5 – C_{10}	Gasoline
C_{10} – C_{18}	Kerosene Jet fuel
C_{15} – C_{25}	Diesel fuel Heating oil Lubricating oil
$>\text{C}_{25}$	Asphalt

This oil rig in Norway is the largest in the world.

been phased out, requiring extensive (and expensive) modifications of engines and of the gasoline refining process.

Coal

Coal has variable composition depending on both its age and location.

Coal was formed from the remains of plants that were buried and subjected to high pressure and heat over long periods of time. Plant materials have a high content of cellulose, a complex molecule whose empirical formula is CH_2O but whose molar mass is around 500,000 g/mol. After the plants and trees that flourished on the earth at various times and places died and were buried, chemical changes gradually lowered the oxygen and hydrogen content of the cellulose molecules. Coal “matures” through four stages: lignite, subbituminous, bituminous, and anthracite. Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio; that is, the relative carbon content gradually increases. Typical elemental compositions of the various coals are given in Table 6.5. The energy available from the combustion of a given mass of coal increases as the carbon content increases. Therefore, anthracite is the most valuable coal, and lignite the least valuable.

Coal is an important and plentiful fuel in the United States, currently furnishing approximately 23% of our energy. As the supply of petroleum dwindles, the share of the energy supply from coal is expected to increase. However, coal is expensive and dangerous to mine underground, and the strip mining of fertile farmland in the Midwest or of scenic land in the West causes obvious problems. In addition, the burning of coal, especially high-sulfur coal, yields air pollutants such as sulfur dioxide, which, in turn, can lead to acid rain, as we learned in Chapter 5. However, even if coal were pure carbon, the carbon dioxide produced when it was burned would still have significant effects on the earth’s climate.

Effects of Carbon Dioxide on Climate

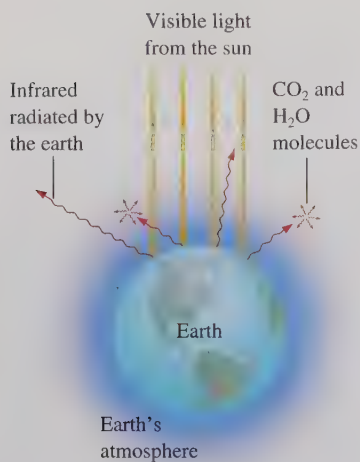
The electromagnetic spectrum, including visible and infrared radiation, is discussed in Chapter 7.

The earth receives a tremendous quantity of radiant energy from the sun, about 30% of which is reflected back into space by the earth’s atmosphere. The remaining energy passes through the atmosphere to the earth’s surface. Some of this energy is absorbed by plants for photosynthesis and some by the oceans to evaporate water, but most of it is absorbed by soil, rocks, and water, increasing the temperature of the earth’s surface. This energy is in turn radiated from the heated surface mainly as *infrared radiation*, often called *heat radiation*.

The atmosphere, like window glass, is transparent to visible light but does not allow all the infrared radiation to pass back into space. Molecules in the atmosphere,

TABLE 6.5 Elemental Composition of Various Types of Coal

Type of Coal	Mass Percent of Each Element				
	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1



The average temperature of the earth's surface is 298 K. It would be 255 K without the "greenhouse gases."

FIGURE 6.12

The earth's atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth's surface is strongly absorbed by CO_2 , H_2O , and other molecules present in smaller amounts (for example, CH_4 and N_2O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

principally H_2O and CO_2 , strongly absorb infrared radiation and radiate it back toward the earth, as shown in Fig. 6.12, so a net amount of thermal energy is retained by the earth's atmosphere, causing the earth to be much warmer than it would be without its atmosphere. In a way, the atmosphere acts like the glass of a greenhouse, which is transparent to visible light but absorbs infrared radiation, thus raising the temperature inside the building. This **greenhouse effect** is seen even more spectacularly on Venus, where the dense atmosphere is thought to be responsible for the high surface temperature of that planet.

Thus the temperature of the earth's surface is controlled to a significant extent by the carbon dioxide and water content of the atmosphere. The effect of atmospheric moisture (humidity) is apparent in the Midwest. In summer, when the humidity is high, the heat of the sun is retained well into the night, giving very high nighttime temperatures. On the other hand, in winter, the coldest temperatures always occur on clear nights, when the low humidity allows efficient radiation of energy back into space.

The atmosphere's water content is controlled by the water cycle (evaporation and precipitation), and the average remains constant over the years. However, as fossil fuels have been used more extensively, the carbon dioxide concentration has increased by about 16% from 1880 to 1980. Comparisons of satellite data have now produced evidence that the greenhouse effect has significantly warmed the earth's atmosphere. The data compare the same areas in both 1979 and 1997. The analysis shows that more infrared radiation was blocked by CO_2 , methane, and other greenhouse gases. This *could* increase the earth's average temperature by as much as 3°C , causing dramatic changes in climate and greatly affecting the growth of food crops.



Sheep grazing on a ranch in Australia.

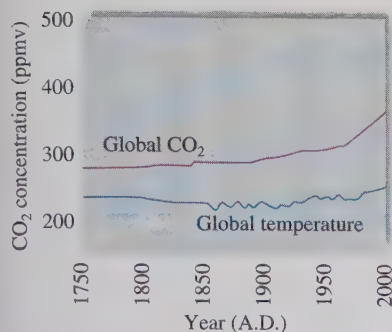


FIGURE 6.13

The atmospheric CO₂ concentration and the average global temperature over the last 250 years. Note the significant increase in CO₂ concentration in the last 50 years.

(Source: National Assessment Synthesis Team, *Climate Change Impacts on the United States: The Potential Consequences of Climate, Variability and Change, Overview, Report for the U.S. Global Change Research Program*, Cambridge University Press, Cambridge UK, p. 13, 2000.)

How well can we predict long-term effects? Because weather has been studied for a period of time that is minuscule compared with the age of the earth, the factors that control the earth's climate in the long range are not clearly understood. For example, we do not understand what causes the earth's periodic ice ages. So it is difficult to estimate the impact of the increasing carbon dioxide levels.

In fact, the variation in the earth's average temperature over the past century is somewhat confusing. In the northern latitudes during the past century, the average temperature rose by 0.8°C over a period of 60 years, then cooled by 0.5°C during the next 25 years, and finally warmed by 0.2°C in the succeeding 15 years. Such fluctuations do not match the steady increase in carbon dioxide. However, in southern latitudes and near the equator during the past century, the average temperature showed a steady rise totaling 0.4°C. This figure is in reasonable agreement with the predicted effect of the increasing carbon dioxide concentration over that period. Another significant fact is that the past 10 years constitute the warmest decade on record.

Although the exact relationship between the carbon dioxide concentration in the atmosphere and the earth's temperature is not known at present, one thing is clear: The increase in the atmospheric concentration of carbon dioxide is quite dramatic (see Fig. 6.13). We must consider the implications of this increase as we consider our future energy needs.

Methane is another greenhouse gas that is 21 times more potent than carbon dioxide. This fact is particularly significant for countries with lots of animals, because methane is produced by methanogenic archae that live in the animals' rumen. For example, sheep and cattle produce about 14% of Australia's total greenhouse emissions. To reduce this level, Australia has initiated a program to vaccinate sheep and cattle to lower the number of archae present in their digestive systems. It is hoped that this effort will reduce by 20% the amount of methane emitted by these animals.

6.6 New Energy Sources

As we search for the energy sources of the future, we need to consider economic, climatic, and supply factors. There are several potential energy sources: the sun (solar), nuclear processes (fission and fusion), biomass (plants), and synthetic fuels. Direct use of the sun's radiant energy to heat our homes and run our factories and transportation systems seems a sensible long-term goal. But what do we do now? Conservation of fossil fuels is one obvious step, but substitutes for fossil fuels also must be found. We will discuss some alternative sources of energy here. Nuclear power will be considered in Chapter 21.

Coal Conversion

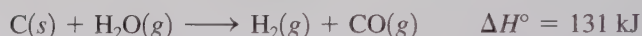
One alternative energy source involves using a traditional fuel—coal—in new ways. Since transportation costs for solid coal are high, more energy-efficient fuels are being developed from coal. One possibility is to produce a gaseous fuel. Substances like coal that contain large molecules have high boiling points and tend to be solids or thick liquids. To convert coal from a solid to a gas therefore requires reducing the size of the molecules; the coal structure must be broken down in a process called *coal gasification*. This is done by treating the coal with oxygen and steam at high

temperatures to break many of the carbon-carbon bonds. These bonds are replaced by carbon-hydrogen and carbon-oxygen bonds as the coal fragments react with the water and oxygen. The process is represented in Fig. 6.14. The desired product is a mixture of carbon monoxide and hydrogen called *synthetic gas*, or **syngas**, and methane (CH_4) gas. Since all the components of this product can react with oxygen to release heat in a combustion reaction, this gas is a useful fuel.

One of the most important considerations in designing an industrial process is efficient use of energy. In coal gasification, some of the reactions are exothermic:



Other gasification reactions are endothermic, for example:



An industrial process must be energy efficient.

If such conditions as the rate of feed of coal, air, and steam are carefully controlled, the correct temperature can be maintained in the process without using any external energy source. That is, an energy balance is maintained.

Presently only a few plants in the United States use syngas produced on site to produce electricity. These plants are being used to evaluate the economic feasibility of producing electrical power by coal gasification.

Although syngas can be used directly as a fuel, it is also important as a raw material to produce other fuels. For example, syngas can be converted directly to methanol:

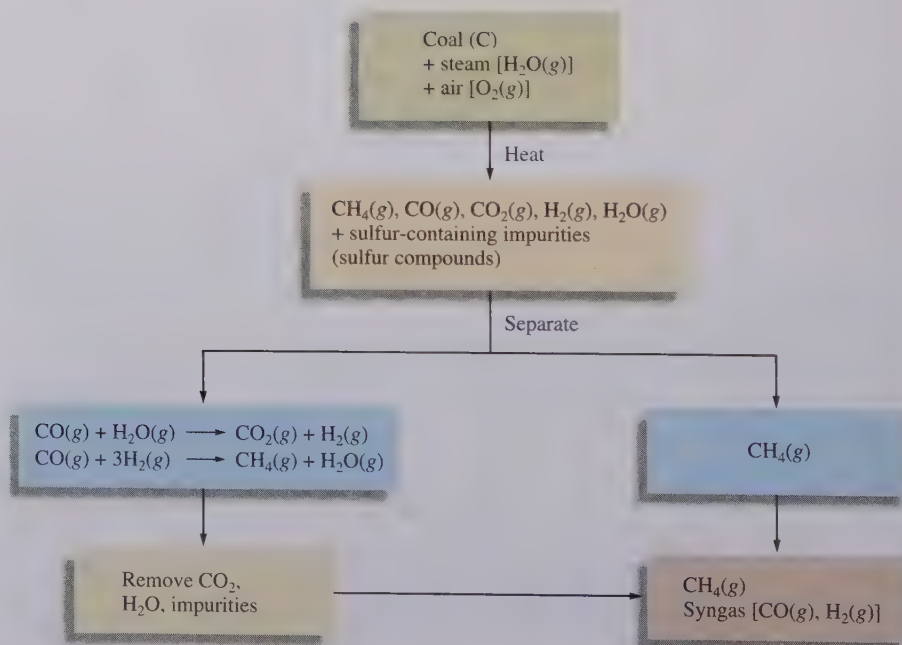
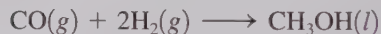


FIGURE 6.14

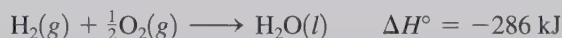
Coal gasification. Reaction of coal with a mixture of steam and air breaks down the large hydrocarbon molecules in the coal to smaller gaseous molecules, which can be used as fuels.

Methanol is used in the production of synthetic fibers and plastics and also can be used as a fuel. In addition, it can be converted directly to gasoline. Approximately half of South Africa's gasoline supply comes from methanol produced from syngas.

In addition to coal gasification, the formation of *coal slurries* is another new use of coal. A slurry is a suspension of fine particles in a liquid, and coal must be pulverized and mixed with water to form a slurry. The slurry can be handled, stored, and burned in ways similar to those used for *residual oil*, a heavy fuel oil from petroleum accounting for almost 15% of U.S. petroleum imports. One hope is that coal slurries might replace solid coal and residual oil as fuels for electricity-generating power plants. However, the water needed for slurries might place an unacceptable burden on water resources, especially in the western states.

Hydrogen as a Fuel

If you have ever seen a lecture demonstration where hydrogen–oxygen mixtures were ignited, or if you have seen a newsfilm or an old photo of the Hindenburg disaster, you have witnessed a demonstration of hydrogen's potential as a fuel. The combustion reaction is



As we saw in Sample Exercise 6.6, the heat of combustion of $\text{H}_2(g)$ per gram is approximately 2.5 times that of natural gas. In addition, hydrogen has a real advantage over fossil fuels in that the only product of hydrogen combustion is water; fossil fuels also produce carbon dioxide. However, even though it appears that hydrogen is a very logical choice as a major fuel for the future, there are three main problems: the cost of production, storage, and transport.

First let's look at the production problem. Although hydrogen is very abundant on earth, virtually none of it exists as the free gas. Currently, the main source of hydrogen gas is from the treatment of natural gas with steam:



We can calculate ΔH for this reaction using Equation (6.1):

$$\begin{aligned} \Delta H^\circ &= \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ \text{ for CO}(g) - \Delta H_f^\circ \text{ for CH}_4(g) - \Delta H_f^\circ \text{ for H}_2\text{O}(g) \\ &= -111 \text{ kJ} - (-75 \text{ kJ}) - (-242 \text{ kJ}) = 206 \text{ kJ} \end{aligned}$$

Note that this reaction is highly endothermic; treating methane with steam is not an efficient way to obtain hydrogen for fuel. It would be much more economical to burn the methane directly.

A virtually inexhaustible supply of hydrogen exists in the waters of the world's oceans. However, the reaction



requires 286 kJ of energy per mole of liquid water, and under current circumstances, large-scale production of hydrogen from water is not economically feasible. However, several methods for such production are currently being studied: electrolysis of water, thermal decomposition of water, thermochemical decomposition of water, and biological decomposition of water.

Electrolysis of water involves passing an electric current through it, as shown in Fig. 1.16 in Chapter 1. The present cost of electricity makes the hydrogen



The main engines in the space shuttle Endeavour use hydrogen and oxygen as fuel.

Electrolysis will be discussed in Chapter 17.

Farming the Wind

In the Midwest the wind blows across fields of corn, soybeans, wheat, and wind turbines—wind turbines? It turns out that the wind that seems to blow almost continuously across the plains is now becoming the latest cash crop. One of these new-breed wind farmers is Daniel Juhl, who recently erected 17 wind turbines on six acres of land near Woodstock, Minnesota. These turbines can generate as much as 10 megawatts (MW) of electricity, which Juhl sells to the local electrical utility.

There is plenty of untapped wind-power in the United States. Wind mappers rate regions on a scale of 1 to 6 (with 6 being the best) to indicate the quality of the wind resource. Wind farms are now being developed in areas rated from 4 to 6. The farmers who own the land welcome the increased income derived from the wind blowing across their land. Economists estimate that each acre devoted to wind turbines can pay royalties to the farmers of as much as \$8000 per year, or many times the revenue from growing corn on that same land. Daniel Juhl claims that farmers who construct the turbines themselves can realize as much as \$20,000 per year per turbine. Globally, wind generation of electricity has nearly quadrupled in the last five years and is expected to increase by about 60% per year in the United States. The economic feasibility of wind-generated electricity has greatly improved in the last 30 years as the wind turbines have

become more efficient. Today's turbines can produce electricity that costs about the same as that from other sources. The most impressive thing about wind power is the magnitude of the supply. According to the American Wind Energy Association in Washington, D.C., the wind-power potential in the United States is comparable or larger than the energy resources under the sands of Saudi Arabia.

The biggest hurdle that must be overcome before wind power can become a significant electricity producer in the United States is construction of the transmission infrastructure—the power lines needed to move the electricity from the rural areas to the cities where most of the power is used. For example, the hundreds of turbines planned in southwest Minnesota in a development called Buffalo Ridge could supply enough electricity to power 1 million homes if transmission problems can be solved.

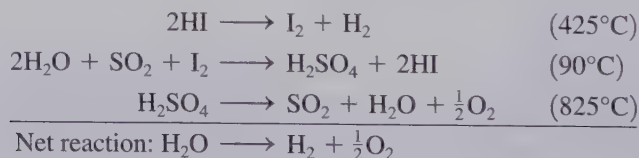
Another possible scenario for wind farms is to use the electrical power generated to decompose water to produce hydrogen gas that could be carried to cities by pipelines and used as a fuel. One real benefit of hydrogen is that it produces water as its only combustion product. Thus, it is essentially pollution-free.

Within a few years wind power could be a major source of electricity. There could be a fresh wind blowing across the energy landscape of the United States in the near future.

produced by electrolysis too expensive to be competitive as a fuel. However, if in the future we develop more efficient sources of electricity, this situation could change.

Thermal decomposition is another method for producing hydrogen from water. This involves heating the water to several thousand degrees, where it spontaneously decomposes into hydrogen and oxygen. However, attaining temperatures in this range would be very expensive even if a practical heat source and a suitable reaction container were available.

In the thermochemical decomposition of water, chemical reactions, as well as heat, are used to “split” water into its components. One such system involves the following reactions (the temperature required for each is given in parentheses):



Note that the HI is not consumed in the net reaction. Note also that the maximum temperature required is 825°C, a temperature that is feasible if a nuclear reactor is used as a heat source. A current research goal is to find a system for which the required temperatures are low enough that sunlight can be used as the energy source.

But what about the organisms that decompose water without the aid of electricity or high temperatures? In the process of photosynthesis, green plants absorb carbon dioxide and water and use them along with energy from the sun to produce the substances needed for growth. Scientists have studied photosynthesis for years, hoping to get answers to humanity's food and energy shortages. At present, much of this research involves attempts to modify the photosynthetic process so that plants will release hydrogen gas from water instead of using the hydrogen to produce complex compounds. Small-scale experiments have shown that under certain conditions plants do produce hydrogen gas, but the yields are far from being commercially useful. At this point the economical production of hydrogen gas remains unrealized.

The storage and transportation of hydrogen also present problems. First, on metal surfaces the H_2 molecule decomposes to atoms. Since the atoms are so small, they can migrate into the metal, causing structural changes that make it brittle. This might lead to a pipeline failure if hydrogen were pumped under high pressure.

A second problem is the relatively small amount of energy that is available *per unit volume* of hydrogen gas. Although the energy available per gram of hydrogen is significantly greater than that per gram of methane, the energy available per given volume of hydrogen is about one-third that available from the same volume of methane. This is demonstrated in Sample Exercise 6.12.

SAMPLE EXERCISE 6.12

Enthalpies of Combustion

Compare the energy available from the combustion of a given volume of methane and the same volume of hydrogen at the same temperature and pressure.

SOLUTION

In Sample Exercise 6.6 we calculated the heat released for the combustion of methane and hydrogen: 55 kJ/g CH_4 and 141 kJ/g H_2 . We also know from our study of gases that 1 mol $H_2(g)$ has the same volume as 1 mol $CH_4(g)$ at the same temperature and pressure (assuming ideal behavior). Thus, for molar volumes of both gases under the same conditions of temperature and pressure,

$$\begin{aligned}
 & \frac{\text{Enthalpy of combustion of 1 molar volume of } H_2(g)}{\text{Enthalpy of combustion of 1 molar volume of } CH_4(g)} \\
 &= \frac{\text{enthalpy of combustion per mole of } H_2}{\text{enthalpy of combustion per mole of } CH_4} \\
 &= \frac{(-141 \text{ kJ/g})(2.02 \text{ g } H_2/\text{mol } H_2)}{(-55 \text{ kJ/g})(16.04 \text{ g } CH_4/\text{mol } CH_4)} \\
 &= \frac{-285}{-882} \approx \frac{1}{3}
 \end{aligned}$$

Thus about three times the volume of hydrogen gas is needed to furnish the same energy as a given volume of methane.

See Exercise 6.72.

Could hydrogen be considered as a potential fuel for automobiles? This is an intriguing question. The internal combustion engines in automobiles can be easily adapted to burn hydrogen. In fact, BMW is now experimenting with a fleet of cars powered by hydrogen-burning internal combustion engines. However, the primary

difficulty is the storage of enough hydrogen to give an automobile a reasonable range. This is illustrated by Sample Exercise 6.13.

SAMPLE EXERCISE 6.13

Comparing Enthalpies of Combustion

Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H_2 (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gal) of gasoline (density = 0.740 g/mL). Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C.

SOLUTION

The mass of 80.0 L gasoline is

$$80.0 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.740 \text{ g}}{\text{mL}} = 59,200 \text{ g}$$

Since H_2 furnishes three times as much energy per gram as gasoline, only a third as much liquid hydrogen is needed to furnish the same energy:

$$\text{Mass of } \text{H}_2(l) \text{ needed} = \frac{59,200 \text{ g}}{3} = 19,700 \text{ g}$$

Since density = mass/volume, then volume = mass/density, and the volume of $\text{H}_2(l)$ needed is

$$\begin{aligned} V &= \frac{19,700 \text{ g}}{0.0710 \text{ g/mL}} \\ &= 2.77 \times 10^5 \text{ mL} = 277 \text{ L} \end{aligned}$$

Thus 277 L of liquid H_2 is needed to furnish the same energy of combustion as 80.0 L of gasoline.

To calculate the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C, we use the ideal gas law:

$$PV = nRT$$

In this case

$$P = 1.00 \text{ atm}, T = 273 + 25^\circ\text{C} = 298 \text{ K}, \text{ and } R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}.$$

Also,

$$n = 19,700 \text{ g-H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g-H}_2} = 9.75 \times 10^3 \text{ mol H}_2$$

Thus

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(9.75 \times 10^3 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1.00 \text{ atm}} \\ &= 2.38 \times 10^5 \text{ L} = 238,000 \text{ L} \end{aligned}$$

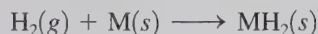
At 1 atm and 25°C, the hydrogen gas needed to replace 20 gal of gasoline occupies a volume of 238,000 L.

See Exercises 6.73 and 6.74.

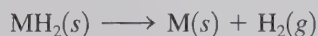
You can see from Sample Exercise 6.13 that an automobile would need a huge tank to hold enough hydrogen gas (at 1 atm) to have a typical mileage range. Clearly, hydrogen must be stored as a liquid or in some other way. Is this feasible? Because of its very low boiling point (20 K), storage of liquid hydrogen requires a superinsulated container that can withstand high pressures. Storage in this manner would be both expensive and hazardous because of the potential for explosion. Thus storage of hydrogen in the individual automobile as a liquid does not seem practical.

Metal hydrides are discussed in Chapter 18.

A much better alternative seems to be the use of metals that absorb hydrogen to form solid metal hydrides:



To use this method of storage, hydrogen gas would be pumped into a tank containing the solid metal in powdered form, where it would be absorbed to form the hydride, whose volume would be little more than that of the metal alone. This hydrogen would then be available for combustion in the engine by release of $\text{H}_2(\text{g})$ from the hydride as needed:



Several types of solids that absorb hydrogen to form hydrides are being studied for use in hydrogen-powered vehicles. The most likely use of hydrogen in automobiles will be to power fuel cells (see Section 17.5). Ford, Honda, and Toyota are all experimenting with cars powered by hydrogen fuel cells.

Other Energy Alternatives

Many other energy sources are being considered for future use. The western states, especially Colorado, contain huge deposits of *oil shale*, which consists of a complex carbon-based material called *kerogen* contained in porous rock formations. These deposits have the potential of being a larger energy source than the vast petroleum deposits of the Middle East. The main problem with oil shale is that the trapped fuel is not fluid and cannot be pumped. To recover the fuel, the rock must be heated to a temperature of 250°C or higher to decompose the kerogen to smaller molecules that produce gaseous and liquid products. This process is expensive and yields large quantities of waste rock, which have a negative environmental impact.

Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is another fuel with the potential to supplement, if not replace, gasoline. The most common method of producing ethanol is fermentation, a process in which sugar is changed to alcohol by the action of yeast. The sugar can come from virtually any source, including fruits and grains, although fuel-grade ethanol would probably come mostly from corn. Car engines can burn pure alcohol or *gasohol*, an alcohol–gasoline mixture (10% ethanol in gasoline), with little modification. Gasohol is now widely available in the United States. The use of pure alcohol as a motor fuel is not feasible in most of the United States because it does not vaporize easily when temperatures are low. However, pure ethanol could be a very practical fuel in warm climates. For example, in Brazil, large quantities of ethanol fuel are being produced for cars.

Methanol (CH_3OH), an alcohol similar to ethanol, which has been used successfully for many years in race cars, is now being evaluated as a motor fuel in California. A major gasoline retailer has agreed to install pumps at 25 locations to dispense a fuel that is 85% methanol and 15% gasoline for use in specially prepared



The sugars in corn are fermented and used to produce ethanol, an additive for gasoline.

CHEMICAL IMPACT

Veggie Gasoline?

Gasoline usage is as high as ever, and world petroleum supplies will eventually dwindle. One possible alternative to petroleum as a source of fuels and lubricants is vegetable oil—the same vegetable oil we now use to cook french fries. Researchers believe that the oils from soybeans, corn, canola, and sunflowers all have the potential to be used in cars as well as on salads.

The use of vegetable oil for fuel is not a new idea. Rudolf Diesel reportedly used peanut oil to run one of his engines at the Paris Exposition in 1900. In addition, ethyl alcohol has been used widely as a fuel in South America and as a fuel additive in the United States.



This promotion bus both advertises biodiesel and demonstrates its usefulness.

automobiles. The California Energy Commission feels that methanol has great potential for providing a secure, long-term energy supply that would alleviate air quality problems. Arizona and Colorado are also considering methanol as a major source of portable energy.

Another potential source of liquid fuels is oil squeezed from seeds (*seed oil*). For example, some farmers in North Dakota, South Africa, and Australia are now using sunflower oil to replace diesel fuel. Oil seeds, found in a wide variety of plants, can be processed to produce an oil composed mainly of carbon and hydrogen, which of course reacts with oxygen to produce carbon dioxide, water, and heat. It is hoped that oil-seed plants can be developed that will thrive under soil and climatic conditions unsuitable for corn and wheat. The main advantage of seed oil as a fuel is that it is renewable. Ideally, fuel would be grown just like food crops.

Key Terms

Section 6.1

energy
law of conservation of energy
potential energy
kinetic energy
heat
work
pathway
state function (property)
system
surroundings
exothermic

For Review

Summary

Energy can be defined as the capacity to do work or to produce heat. The law of conservation of energy (or the first law of thermodynamics) states that energy can be converted from one form to another, but it cannot be created or destroyed. Heat is a means for the transfer of energy. Chemical reactions can either evolve or absorb heat, depending on whether the potential energy stored in the bonds of the reactant molecules is greater or less than the energy stored in the bonds of the product molecules.

When a reaction evolves heat, it is said to be exothermic; a reaction that absorbs heat from its surroundings is endothermic. Energy is a state function; that

Biodiesel, a fuel made by esterifying the fatty acids found in vegetable oil, has some real advantages over regular diesel fuel. Biodiesel produces fewer pollutants such as particulates, carbon monoxide, and complex organic molecules, and since vegetable oils have no sulfur, there is no noxious sulfur dioxide in the exhaust gases. Also, biodiesel can run in existing engines with little modification. In addition, biodiesel is much more biodegradable than petroleum-based fuels, so spills cause less environmental damage.

Of course, biodiesel also has some serious drawbacks. The main one is that it costs about three times as much as regular diesel fuel. Biodiesel also produces more nitrogen oxides in the exhaust than conventional diesel fuel and is less stable in storage. Biodiesel also can leave more gummy deposits in engines and must be “winterized” by removing components that tend to solidify at low temperatures.

The best solution may be to use biodiesel as an additive to regular diesel fuel. One such fuel is known as B20 because it is 20% biodiesel and 80% conventional diesel fuel. B20 is especially attractive because of the higher lubricating ability of vegetable oils, thus reducing diesel engine wear.

Vegetable oils are also being looked at as replacements for motor oils and hydraulic fluids. Tests of a sunflower seed-based engine lubricant manufactured by Renewable Lubricants of Hartville, Ohio, have shown satisfactory lubricating ability while lowering particle emissions. In addition, Lou Honary and his colleagues at the University of Northern Iowa have developed BioSOY, a vegetable oil-based hydraulic fluid for use in heavy machinery.

Veggie oil fuels and lubricants seem to have a growing market as petroleum supplies wane and as environmental laws become more stringent. In Germany’s Black Forest region, for example, environmental protection laws require that farm equipment use only vegetable oil fuels and lubricants. In the near future there may be veggie oil in your garage as well as in your kitchen.

Adapted from “Fill ‘Er Up . . . with Veggie Oil,” by Corinna Wu, as appeared in *Science News*, Vol. 154, December 5, 1998, p. 364.

endothermic
thermodynamics
first law of thermodynamics
internal energy

Section 6.2

enthalpy
calorimeter
calorimetry
heat capacity
specific heat capacity
molar heat capacity
constant-pressure calorimetry
constant-volume calorimetry

Section 6.3

Hess’s law

Section 6.4

standard enthalpy of formation
standard state

Section 6.5

fossil fuels
petroleum
natural gas
coal
greenhouse effect

Section 6.6

syngas

is, a change in energy in going from one state to another is independent of the pathway.

Heat flow associated with a chemical reaction is measured by calorimetry, a technique that involves measuring temperature changes when a body absorbs or discharges heat. For a process carried out at constant pressure, the heat flow equals the change in enthalpy (ΔH).

Since enthalpy is a state function, the change in enthalpy in going from a given set of reactants to a given set of products is the same regardless of whether the reaction takes place in one step or in a series of steps (a principle known as Hess’s law). We can therefore calculate the enthalpy change for an overall reaction by summing the ΔH values from a series of steps that yield that net reaction. Also, it is often convenient to calculate the ΔH° value for a reaction from values for the standard enthalpies of formation (ΔH_f°) of the reactants and products. The standard enthalpy of formation is the enthalpy change that accompanies the formation of one mole of a compound from its elements, where all substances are in their standard states. For a given reaction,

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

The practical aspects of energy production from fossil fuels involve problems of supply and environmental impact. The combustion of carbon-based fuels produces carbon dioxide, which is involved, along with atmospheric water, in controlling the surface temperature of the earth. Increased carbon dioxide concentration in the atmosphere may produce gradual global warming due to the greenhouse effect. Alternative fuels, such as syngas from coal, hydrogen from breakdown of water, and ethanol from the fermentation of sugar, are being studied as replacements for petroleum products.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

- Objects placed together eventually reach the same temperature. When you go into a room and touch a piece of metal in that room, it feels colder than a piece of plastic. Explain.
- What is meant by the term *lower in energy*? Which is lower in energy, a mixture of hydrogen and oxygen gases or liquid water? How do you know? Which of the two is more stable? How do you know?
- A fire is started in a fireplace by striking a match and lighting crumpled paper under some logs. Explain all the energy transfers in this scenario using the terms *exothermic*, *endothermic*, *system*, *surroundings*, *potential energy*, and *kinetic energy* in the discussion.
- Liquid water turns to ice. Is this process endothermic or exothermic? Explain what is occurring using the terms *system*, *surroundings*, *heat*, *potential energy*, and *kinetic energy* in the discussion.
- Consider the following statements: "Heat is a form of energy, and energy is conserved. The heat lost by a system must be equal to the amount of heat gained by the surroundings. Therefore, heat is conserved." Indicate everything you think is correct in these statements. Indicate everything you think is incorrect. Correct the incorrect statements and explain.
- Consider 5.5 L of a gas at a pressure of 3.0 atm in a cylinder with a movable piston. The external pressure is changed so that the volume changes to 10.5 L.
 - Calculate the work done, and indicate the correct sign.
 - Use the preceding data but consider the process to occur in two steps. At the end of the first step, the volume is 7.0 L. The second step results in a final volume of 10.5 L. Calculate the work done, and indicate the correct sign.
 - Calculate the work done if after the first step the volume is 8.0 L and the second step leads to a volume of 10.5 L. Does the work differ from that in part b? Explain.
- In Question 6 the work calculated for the different conditions in the various parts of the question was different even though the system had the same initial and final conditions. Based on this information, is work a state function?
 - Explain how you know that work is not a state function.
 - Why does the work increase with an increase in the number of steps?
 - Which two-step process resulted in more work, when the first step had the bigger change in volume or when the second step had the bigger change in volume? Explain.
- Photosynthetic plants use the following reaction to produce glucose, cellulose, and so forth:

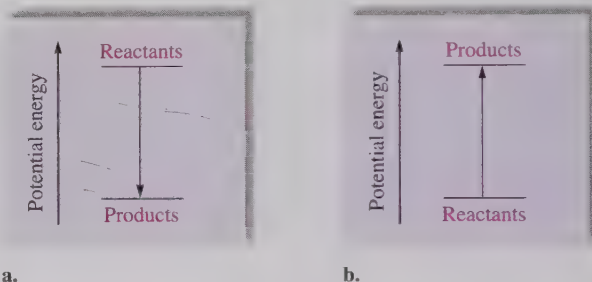


How might extensive destruction of forests exacerbate the greenhouse effect?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- Explain why ΔH is obtained directly from a coffee-cup calorimeter, whereas ΔE is obtained directly from a bomb calorimeter.
- Consider the following potential energy diagrams for two different reactions.



- Which plot represents an exothermic reaction? In plot a, do the reactants on average have stronger or weaker bonds than the products? In plot b, reactants must gain potential energy to convert to products. How does this occur?
- High-quality audio amplifiers generate large amounts of heat. To dissipate the heat and prevent damage to the electronic components, heat-radiating metal fins are used. Would it be better to make these fins out of iron or aluminum? Why? (See Table 6.1 for specific heat capacities.)
 - Predict the signs of q and w for the process of boiling water.
 - What is a state function? Enthalpy and internal energy are state functions as a direct consequence of the first law of thermodynamics. Explain.
 - Hess's law is really just another statement of the first law of thermodynamics. Explain.
 - What is the purpose for defining standard enthalpies of formation?
 - Explain the advantages and disadvantages of hydrogen as an alternative fuel.

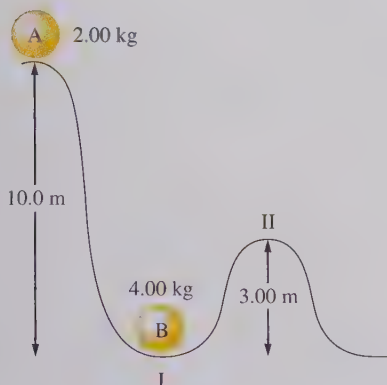
Exercises

In this section similar exercises are paired.

Potential and Kinetic Energy

- Calculate the kinetic energy of a baseball (mass = 5.25 oz) with a velocity of 1.0×10^2 mi/h.

18. Calculate the kinetic energy of a 1.0×10^{-5} -g object with a velocity of 2.0×10^5 cm/s.
19. Which has the greater kinetic energy, an object with a mass of 2.0 kg and a velocity of 1.0 m/s or an object with a mass of 1.0 kg and a velocity of 2.0 m/s?
20. Consider the accompanying diagram. Ball A is allowed to fall and strike ball B. Assume that all of ball A's energy is transferred to ball B, at point I, and that there is no loss of energy to other sources. What is the kinetic energy and the potential energy of ball B at point II? The potential energy is given by $PE = mgz$, where m is the mass in kilograms, g is the gravitational constant (9.80 m/s^2), and z is the distance in meters.



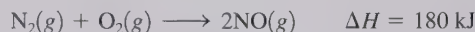
Heat and Work

21. Calculate ΔE for each of the following cases.
- $q = +51 \text{ kJ}$, $w = -15 \text{ kJ}$
 - $q = +100. \text{ kJ}$, $w = -65 \text{ kJ}$
 - $q = -65 \text{ kJ}$, $w = -20. \text{ kJ}$
 - In which of these cases does the system do work on the surroundings?
22. Calculate ΔE for each of the following.
- $q = -47 \text{ kJ}$, $w = +88 \text{ kJ}$
 - $q = +82 \text{ kJ}$, $w = +47 \text{ kJ}$
 - $q = +47 \text{ kJ}$, $w = 0$
 - In which of these cases do the surroundings do work on the system?
23. A system releases 125 kJ of heat while 104 kJ of work is done on it. Calculate ΔE .
24. A system undergoes a process consisting of the following two steps:
- Step 1: The system absorbs 72 J of heat while 35 J of work is done on it.
- Step 2: The system absorbs 35 J of heat while performing 72 J of work.
- Calculate ΔE for the overall process.

25. The volume of an ideal gas is decreased from 5.0 L to 5.0 mL at a constant pressure of 2.0 atm. Calculate the work associated with this process.
26. Consider a mixture of air and gasoline vapor in a cylinder with a piston. The original volume is 40. cm^3 . If the combustion of this mixture releases 950. J of energy, to what volume will the gases expand against a constant pressure of 650. torr if all the energy of combustion is converted into work to push back the piston?
27. A balloon filled with 39.1 mol helium has a volume of 876 L at 0.0°C and 1.00 atm pressure. The temperature of the balloon is increased to 38.0°C as it expands to a volume of 998 L, the pressure remaining constant. Calculate q , w , and ΔE for the helium in the balloon. (The molar heat capacity for helium gas is $20.8 \text{ J/}^\circ\text{C} \cdot \text{mol}$.)
28. One mole of $\text{H}_2\text{O(g)}$ at 1.00 atm and $100.^\circ\text{C}$ occupies a volume of 30.6 L. When one mole of $\text{H}_2\text{O(g)}$ is condensed to one mole of $\text{H}_2\text{O(l)}$ at 1.00 atm and $100.^\circ\text{C}$, 40.66 kJ of heat is released. If the density of $\text{H}_2\text{O(l)}$ at this temperature and pressure is 0.996 g/cm^3 , calculate ΔE for the condensation of one mole of water at 1.00 atm and $100.^\circ\text{C}$.

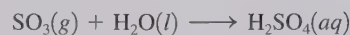
Properties of Enthalpy

29. One of the components of polluted air is NO. It is formed in the high-temperature environment of internal combustion engines by the following reaction:



Why are high temperatures needed to convert N_2 and O_2 to NO?

30. The reaction



is the last step in the commercial production of sulfuric acid. The enthalpy change for this reaction is -227 kJ . In designing a sulfuric acid plant, is it necessary to provide for heating or cooling of the reaction mixture? Explain.

31. Are the following processes exothermic or endothermic?
- When solid KBr is dissolved in water, the solution gets colder.
 - Natural gas (CH_4) is burned in a furnace.
 - When concentrated H_2SO_4 is added to water, the solution gets very hot.
 - Water is boiled in a teakettle.
32. Are the following processes exothermic or endothermic?
- the combustion of gasoline in a car engine
 - water condensing on a cold pipe
 - $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$
 - $\text{F}_2(\text{g}) \longrightarrow 2\text{F}(\text{g})$
33. The overall reaction in commercial heat packs can be represented as



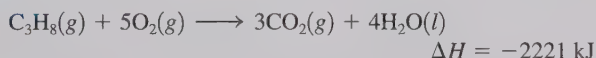
- How much heat is released when 4.00 mol iron is reacted with excess O_2 ?
- How much heat is released when 1.00 mol Fe_2O_3 is produced?
- How much heat is released when 1.00 g iron is reacted with excess O_2 ?
- How much heat is released when 10.0 g Fe and 2.00 g O_2 are reacted?

34. Consider the following reaction:



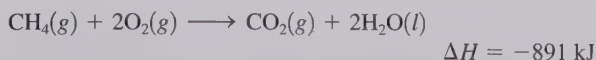
- How much heat is evolved for the production of 1.00 mol of $\text{H}_2\text{O}(l)$?
- How much heat is evolved when 4.03 g of hydrogen is reacted with excess oxygen?
- How much heat is evolved when 186 g of oxygen is reacted with excess hydrogen?
- The total volume of hydrogen gas needed to fill the Hindenburg was $2.0 \times 10^8 \text{ L}$ at 1.0 atm and 25°C . How much heat was evolved when the Hindenburg exploded, assuming all of the hydrogen reacted?

35. Consider the combustion of propane:



Assume that all the heat in Sample Exercise 6.3 comes from the combustion of propane. What mass of propane must be burned to furnish this amount of energy assuming the heat transfer process is 60.% efficient?

36. Consider the following reaction:



Calculate the enthalpy change for each of the following cases:

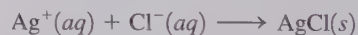
- 1.00 g methane is burned in excess oxygen.
- $1.00 \times 10^3 \text{ L}$ methane gas at 740. torr and 25°C is burned in excess oxygen.

Calorimetry and Heat Capacity

- Consider the substances in Table 6.1. Which substance requires the largest amount of energy to raise the temperature of 25.0 g of the substance from 15.0°C to 37.0°C ? Calculate the energy. Which substance in Table 6.1 has the largest temperature change when 550. g of the substance absorbs 10.7 kJ of energy? Calculate the temperature change.
- The specific heat capacity of silver is $0.24 \text{ J/}^\circ\text{C} \cdot \text{g}$.
 - Calculate the energy required to raise the temperature of 150.0 g Ag from 273 K to 298 K.
 - Calculate the energy required to raise the temperature of 1.0 mol Ag by 1.0°C (called the *molar heat capacity* of silver).

- It takes 1.25 kJ of energy to heat a sample of pure silver from 12.0°C to 15.2°C . Calculate the mass of the sample of silver.

- It takes 78.2 J to raise the temperature of 45.6 g lead by 13.3°C . Calculate the specific heat capacity and molar heat capacity of lead.
- It takes 585 J of energy to raise the temperature of 125.6 g mercury from 20.0°C to 53.5°C . Calculate the specific heat capacity and the molar heat capacity of mercury.
- A 30.0-g sample of water at 280. K is mixed with 50.0 g of water at 330. K. Calculate the final temperature of the mixture assuming no heat loss to the surroundings.
- A 5.00-g sample of aluminum pellets (specific heat capacity = $0.89 \text{ J/}^\circ\text{C} \cdot \text{g}$) and a 10.00-g sample of iron pellets (specific heat capacity = $0.45 \text{ J/}^\circ\text{C} \cdot \text{g}$) are heated to 100.0°C . The mixture of hot iron and aluminum is then dropped into 97.3 g of water at 22.0°C . Calculate the final temperature of the metal and water mixture, assuming no heat loss to the surroundings.
- A 150.0-g sample of a metal at 75.0°C is added to 150.0 g of H_2O at 15.0°C . The temperature of the water rises to 18.3°C . Calculate the specific heat capacity of the metal, assuming that all the heat lost by the metal is gained by the water.
- A 110.-g sample of copper (specific heat capacity = $0.20 \text{ J/}^\circ\text{C} \cdot \text{g}$) is heated to 82.4°C and then placed in a container of water at 22.3°C . The final temperature of the water and copper is 24.9°C . What is the mass of the water in the container, assuming that all the heat lost by the copper is gained by the water?
- In a coffee-cup calorimeter, 50.0 mL of 0.100 M AgNO_3 and 50.0 mL of 0.100 M HCl are mixed to yield the following reaction:



The two solutions were initially at 22.60°C , and the final temperature is 23.40°C . Calculate the heat that accompanies this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$.

- In a coffee-cup calorimeter, 1.60 g of NH_4NO_3 is mixed with 75.0 g of water at an initial temperature of 25.00°C . After dissolution of the salt, the final temperature of the calorimeter contents is 23.34°C . Assuming the solution has a heat capacity of $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$ and assuming no heat loss to the calorimeter, calculate the enthalpy change for the dissolution of NH_4NO_3 in units of kJ/mol.
- Consider the dissolution of CaCl_2 :



An 11.0-g sample of CaCl_2 is dissolved in 125 g of water, with both substances at 25.0°C . Calculate the final temperature of the solution assuming no heat lost to the surround-

ings and assuming the solution has a specific heat capacity of $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$.

48. Consider the reaction



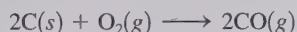
Calculate the heat when 100.0 mL of 0.500 M HCl is mixed with 300.0 mL of 0.100 M Ba(OH)₂. Assuming that the temperature of both solutions was initially 25.0°C and that the final mixture has a mass of 400.0 g and a specific heat capacity of $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$, calculate the final temperature of the mixture.

49. The combustion of 0.1584 g benzoic acid increases the temperature of a bomb calorimeter by 2.54°C . Calculate the heat capacity of this calorimeter. (The energy released by combustion of benzoic acid is 26.42 kJ/g .) A 0.2130-g sample of vanillin ($\text{C}_8\text{H}_8\text{O}_3$) is then burned in the same calorimeter, and the temperature increases by 3.25°C . What is the energy of combustion per gram of vanillin? Per mole of vanillin?

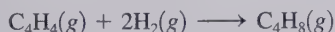
50. A 0.1964-g sample of quinone ($\text{C}_6\text{H}_4\text{O}_2$) is burned in a bomb calorimeter that has a heat capacity of $1.56 \text{ kJ/}^\circ\text{C}$. The temperature of the calorimeter increases by 3.2°C . Calculate the energy of combustion of quinone per gram and per mole.

Hess's Law

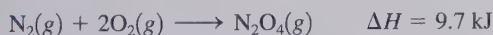
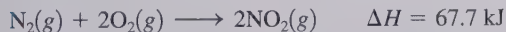
51. The enthalpy of combustion of solid carbon to form carbon dioxide is -393.7 kJ/mol carbon, and the enthalpy of combustion of carbon monoxide to form carbon dioxide is -283.3 kJ/mol CO. Use these data to calculate ΔH for the reaction



52. Combustion reactions involve reacting a substance with oxygen. When compounds containing carbon and hydrogen are combusted, carbon dioxide and water are the products. Using the enthalpies of combustion for C_4H_4 (-2341 kJ/mol), C_4H_8 (-2755 kJ/mol), and H_2 (-286 kJ/mol), calculate ΔH for the reaction



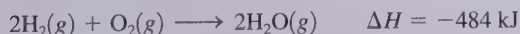
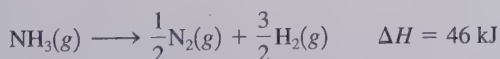
53. Given the following data



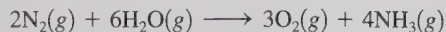
calculate ΔH for the dimerization of NO_2 :



54. Given the following data

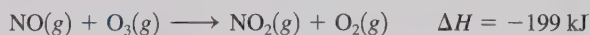
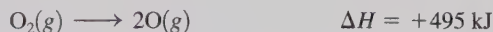
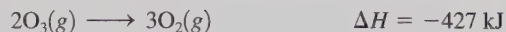


calculate ΔH for the reaction

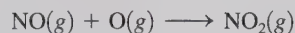


On the basis of the enthalpy change, is this a useful reaction for the synthesis of ammonia?

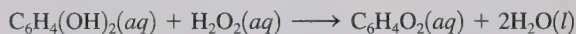
55. Given the following data



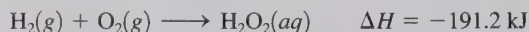
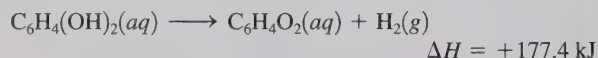
calculate ΔH for the reaction



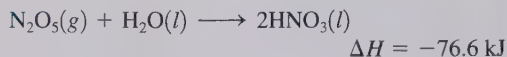
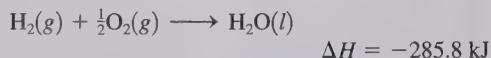
56. The bombardier beetle uses an explosive discharge as a defensive measure. The chemical reaction involved is the oxidation of hydroquinone by hydrogen peroxide to produce quinone and water:



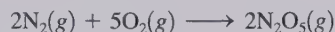
Calculate ΔH for this reaction from the following data:



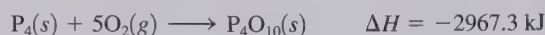
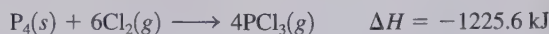
57. Given the following data



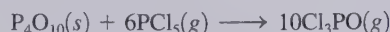
calculate the ΔH for the reaction



58. Given the following data



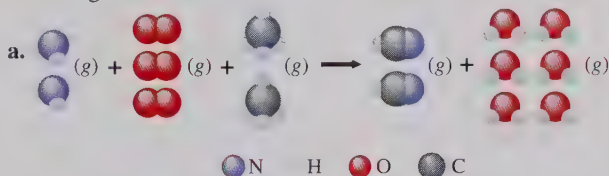
calculate ΔH for the reaction



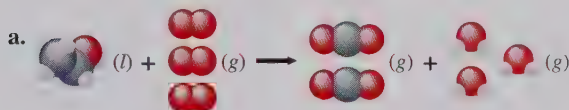
Standard Enthalpies of Formation

59. Give the definition of the standard enthalpy of formation for a substance. Write separate reactions for the formation of NaCl , H_2O , $\text{C}_6\text{H}_{12}\text{O}_6$, and PbSO_4 that have ΔH_f° values equal to ΔH_f° for each compound.
60. Write reactions for which the enthalpy change will be
- ΔH_f° for solid aluminum oxide.
 - The standard enthalpy of combustion of liquid ethanol, $\text{C}_2\text{H}_5\text{OH}(l)$.
 - The standard enthalpy of neutralization of sodium hydroxide solution by hydrochloric acid.
 - ΔH_f° for gaseous vinyl chloride, $\text{C}_2\text{H}_3\text{Cl}(g)$.
 - The enthalpy of combustion of liquid benzene, $\text{C}_6\text{H}_6(l)$.
 - The enthalpy of solution of solid ammonium bromide.

61. Use the values of ΔH_f° in Appendix 4 to calculate ΔH° for the following reactions.

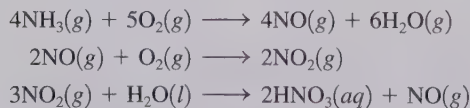


- b. $\text{Ca}_3(\text{PO}_4)_2(s) + 3\text{H}_2\text{SO}_4(l) \longrightarrow 3\text{CaSO}_4(s) + 2\text{H}_3\text{PO}_4(l)$
- c. $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
62. Use the values of ΔH_f° in Appendix 4 to calculate ΔH° for the following reactions. (See Exercise 61.)

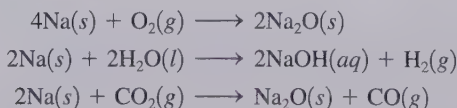


- b. $\text{SiCl}_4(l) + 2\text{H}_2\text{O}(l) \longrightarrow \text{SiO}_2(s) + 4\text{HCl}(aq)$
- c. $\text{MgO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Mg}(\text{OH})_2(s)$

63. The Ostwald process for the commercial production of nitric acid from ammonia and oxygen involves the following steps:



- a. Use the values of ΔH_f° in Appendix 4 to calculate the value of ΔH° for each of the preceding reactions.
- b. Write the overall equation for the production of nitric acid by the Ostwald process by combining the preceding equations. (Water is also a product.) Is the overall reaction exothermic or endothermic?
64. Calculate ΔH° for each of the following reactions using the data in Appendix 4:



Explain why a water or carbon dioxide fire extinguisher might not be effective in putting out a sodium fire.

65. The reusable booster rockets of the space shuttle use a mixture of aluminum and ammonium perchlorate as fuel. A possible reaction is



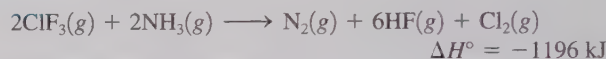
Calculate ΔH° for this reaction.

66. The space shuttle orbiter utilizes the oxidation of methyl hydrazine by dinitrogen tetroxide for propulsion:



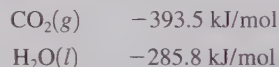
Calculate ΔH° for this reaction.

67. Consider the reaction



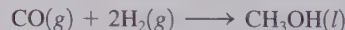
Calculate ΔH_f° for $\text{ClF}_3(g)$.

68. The standard enthalpy of combustion of ethene gas, $\text{C}_2\text{H}_4(g)$, is -1411.1 kJ/mol at 298 K. Given the following enthalpies of formation, calculate ΔH_f° for $\text{C}_2\text{H}_4(g)$.



Energy Consumption and Sources

69. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) has been proposed as an alternative fuel. Calculate the standard of enthalpy of combustion per gram of liquid ethanol.
70. Syngas can be burned directly or converted to methanol. Calculate ΔH° for the reaction

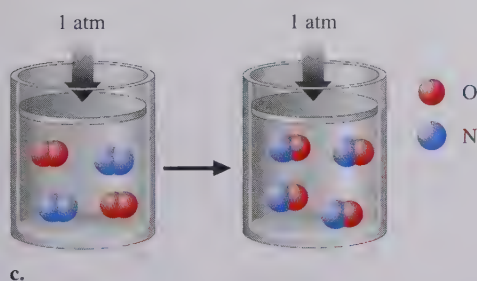
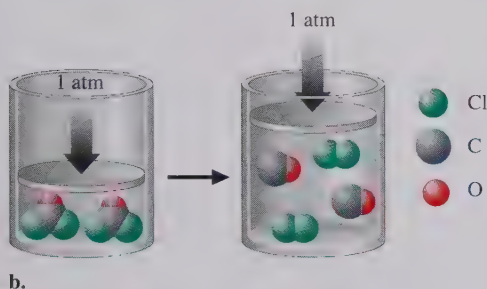
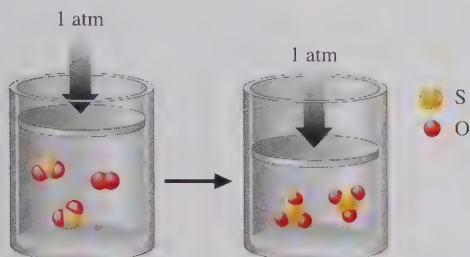


71. Some automobiles and buses have been equipped to burn propane (C_3H_8). Compare the amounts of energy that can be obtained per gram of $\text{C}_3\text{H}_8(g)$ and per gram of gasoline, assuming that gasoline is pure octane, $\text{C}_8\text{H}_{18}(l)$. (See Sample Exercise 6.11.) Look up the boiling point of propane. What disadvantages are there to using propane instead of gasoline as a fuel?
72. Acetylene (C_2H_2) and butane (C_4H_{10}) are gaseous fuels with enthalpies of combustion of -49.9 kJ/g and -49.5 kJ/g , respectively. Compare the energy available from the combustion of a given volume of acetylene to the combustion energy from the same volume of butane at the same temperature and pressure.
73. Assume that $4.19 \times 10^6 \text{ kJ}$ of energy is needed to heat a home. If this energy is derived from the combustion of methane (CH_4), what volume of methane, measured at STP, must be burned? ($\Delta H_{\text{combustion}}^\circ$ for $\text{CH}_4 = -891 \text{ kJ/mol}$)

74. The complete combustion of acetylene, $\text{C}_2\text{H}_2(\text{g})$, produces 1300. kJ of energy per mole of acetylene consumed. How many grams of acetylene must be burned to produce enough heat to raise the temperature of 1.00 gal of water by 10.0°C if the process is 80.0% efficient? Assume the density of water is 1.00 g/cm^3 .

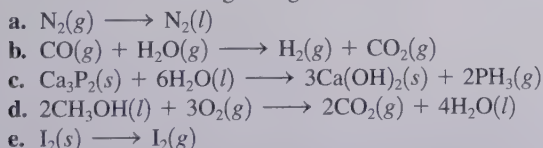
Additional Exercises

75. Three gas-phase reactions were run in a constant-pressure piston apparatus as illustrated below. For each reaction, give the balanced reaction and predict the sign of w (the work done) for the reaction.



If just the balanced reactions were given, how could you predict the sign of w for a reaction?

76. Consider the following changes:



At constant temperature and pressure, in which of these changes is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?

77. Consider the following cyclic process carried out in two steps on a gas:

Step 1: 45 J of heat is added to the gas, and 10. J of expansion work is performed.

Step 2: 60. J of heat is removed from the gas as the gas is compressed back to the initial state.

Calculate the work for the gas compression in Step 2.

78. A sample of an ideal gas at 15.0 atm and 10.0 L is allowed to expand against a constant external pressure of 2.00 atm at a constant temperature. Calculate the work in units of kJ for the gas expansion.
79. A biology experiment requires the preparation of a water bath at 37.0°C (body temperature). The temperature of the cold tap water is 22.0°C , and the temperature of the hot tap water is 55.0°C . If a student starts with 90.0 g of cold water, what mass of hot water must be added to reach 37.0°C ?

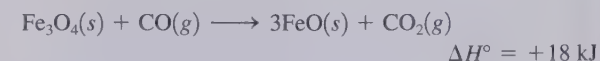
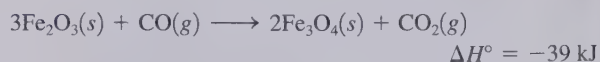
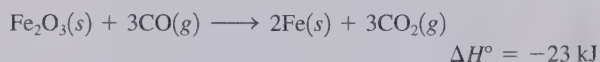
80. Calculate ΔH° for the reaction



A 5.00-g chunk of potassium is dropped into 1.00 kg water at 24.0°C . What is the final temperature of the water after the preceding reaction occurs? Assume that all the heat is used to raise the temperature of the water. (Never run this reaction. It is very dangerous; it bursts into flame!)

81. The enthalpy of neutralization for the reaction of a strong acid with a strong base is -56 kJ/mol of water produced. How much energy will be released when 200.0 mL of 0.400 M HCl is mixed with 150.0 mL of 0.500 M NaOH?
82. In a bomb calorimeter, the reaction vessel is surrounded by water that must be added for each experiment. Since the amount of water is not constant from experiment to experiment, the mass of water must be measured in each case. The heat capacity of the calorimeter is broken down into two parts: the water and the calorimeter components. If a calorimeter contains 1.00 kg water and has a total heat capacity of $10.84 \text{ kJ/}^\circ\text{C}$, what is the heat capacity of the calorimeter components?
83. The bomb calorimeter in Exercise 82 is filled with 987 g of water. The initial temperature of the calorimeter contents is 23.32°C . A 1.056-g sample of benzoic acid ($\Delta E_{\text{comb}} = -26.42 \text{ kJ/g}$) is combusted in the calorimeter. What is the final temperature of the calorimeter contents?

84. Given the following data

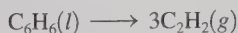


calculate ΔH° for the reaction



85. At 298 K, the standard enthalpies of formation for $\text{C}_2\text{H}_2(\text{g})$ and $\text{C}_6\text{H}_6(\text{l})$ are 227 kJ/mol and 49 kJ/mol, respectively.

a. Calculate ΔH° for



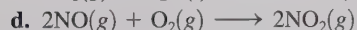
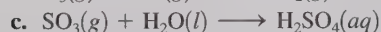
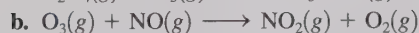
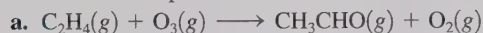
b. Both acetylene (C_2H_2) and benzene (C_6H_6) can be used as fuels. Which compound would liberate more energy per gram when combusted in air?

86. Given the following data



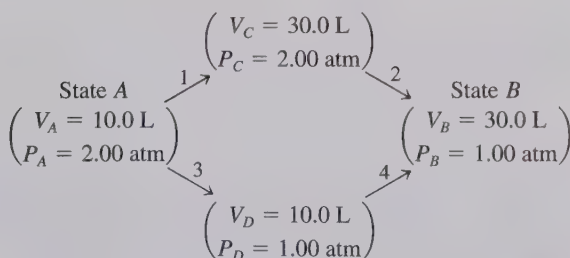
calculate the standard enthalpy of formation for $\text{CuO}(\text{s})$.

87. Calculate ΔH° for each of the following reactions, which occur in the atmosphere.

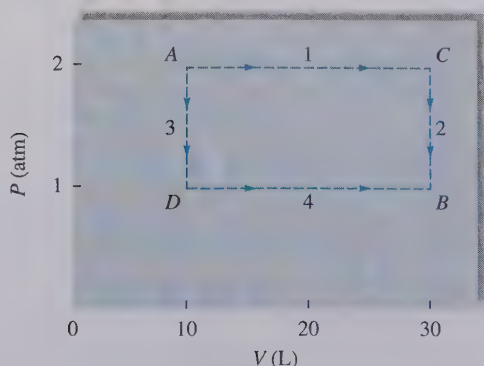


Challenge Problems

88. Consider 2.00 mol of an ideal gas that is taken from state A ($P_A = 2.00 \text{ atm}$, $V_A = 10.0 \text{ L}$) to state B ($P_B = 1.00 \text{ atm}$, $V_B = 30.0 \text{ L}$) by two different pathways:



These pathways are summarized on the following graph of P versus V :



Calculate the work (in units of J) associated with the two pathways. Is work a state function? Explain.

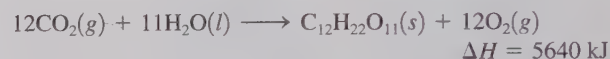
89. Combustion of table sugar produces $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. When 1.46 g of table sugar is combusted in a constant-volume (bomb) calorimeter, 24.00 kJ of heat is liberated.

a. Assuming that table sugar is pure sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$, write the balanced equation for the combustion reaction.

b. Calculate ΔE in kJ/mol $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ for the combustion reaction of sucrose.

c. Calculate ΔH in kJ/mol $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ for the combustion reaction of sucrose at 25°C .

90. The sun supplies energy at a rate of about 1.0 kilowatt per square meter of surface area (1 watt = 1 J/s). The plants in an agricultural field produce the equivalent of 20. kg of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per hour per hectare (1 ha = 10,000 m^2). Assuming that sucrose is produced by the reaction



calculate the percentage of sunlight used to produce the sucrose—that is, determine the efficiency of photosynthesis.

91. The best solar panels currently available are about 13% efficient in converting sunlight to electricity. A typical home will use about 40. kWh of electricity per day (1 kWh = 1 kilowatt hour; 1 kW = 1000 J/s). Assuming 8.0 hours of useful sunlight per day, calculate the minimum solar panel surface area necessary to provide all of a typical home's electricity. (See Exercise 90 for the energy rate supplied by the sun.)

92. On Easter Sunday, April 3, 1983, nitric acid spilled from a tank car near downtown Denver, Colorado. The spill was neutralized with sodium carbonate:

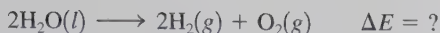


a. Calculate ΔH° for this reaction. Approximately 2.0×10^4 gal nitric acid was spilled. Assume that the acid was an aqueous solution containing 70.0% HNO_3 by mass with a density of 1.42 g/cm^3 . How much sodium carbonate was required for complete neutralization of the spill, and how much heat was evolved? (ΔH_f° for $\text{NaNO}_3(\text{aq}) = -467 \text{ kJ/mol}$)

b. According to *The Denver Post* for April 4, 1983, authorities feared that dangerous air pollution might occur during the neutralization. Considering the magnitude of ΔH° , what was their major concern?

93. A piece of chocolate cake contains about 400 Calories. A nutritional Calorie is equal to 1000 calories (thermochemical calories), which is equal to 4.184 kJ. How many 8-in-high steps must a 180-lb man climb to expend the 400 Cal from the piece of cake? See Exercise 20 for the formula for potential energy.

94. The standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ at 298 K is -285.8 kJ/mol . Calculate the change in internal energy for the following reaction at 298 K and 1.00 atm:



Hint: Using the ideal gas equation, derive an expression for work in terms of n , R , and T .

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

95. A sample consisting of 22.7 g of a nongaseous, unstable compound X is placed inside a metal cylinder with a radius of 8.00 cm, and a piston is carefully placed on the surface of the compound so that, for all practical purposes, the distance between the bottom of the cylinder and the piston is zero. (A hole in the piston allows trapped air to escape as the piston is placed on the compound; then this hole is plugged so that nothing inside the cylinder can escape.) The piston-and-cylinder apparatus is carefully placed in 10.00 kg of water at 25.00°C. The barometric pressure is 778 torr.

When the compound spontaneously decomposes, the piston moves up, the temperature of the water reaches a maximum of 29.52°C, and then it gradually decreases as the water loses heat to the surrounding air. The distance between the piston and the bottom of the cylinder, at the maximum temperature, is 59.8 cm. Chemical analysis shows that the cylinder contains 0.300 mol carbon dioxide, 0.250 mol liquid water, 0.025 mol oxygen gas, and an undetermined amount of a gaseous element A.

It is known that the enthalpy change for the decomposition of X, according to the reaction described above, is -1893 kJ/mol X . The standard enthalpies of formation for gaseous carbon dioxide and liquid water are -393.5 kJ/mol and -286 kJ/mol , respectively. The heat capacity for water is $4.184 \text{ J/}^\circ\text{C} \cdot \text{g}$. The conversion factor between $\text{L} \cdot \text{atm}$ and J can be determined from the two values for the gas constant R , namely, $0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$ and $8.3145 \text{ J/mol} \cdot \text{K}$. The vapor pressure of water at 29.5°C is 31 torr. Assume that the heat capacity of the piston-and-cylinder apparatus is negligible and that the piston has negligible mass.

Given the preceding information, determine

- The formula for X.
- The pressure–volume work (in kJ) for the decomposition of the 22.7-g sample of X.
- The molar change in internal energy for the decomposition of X and the approximate standard enthalpy of formation for X.



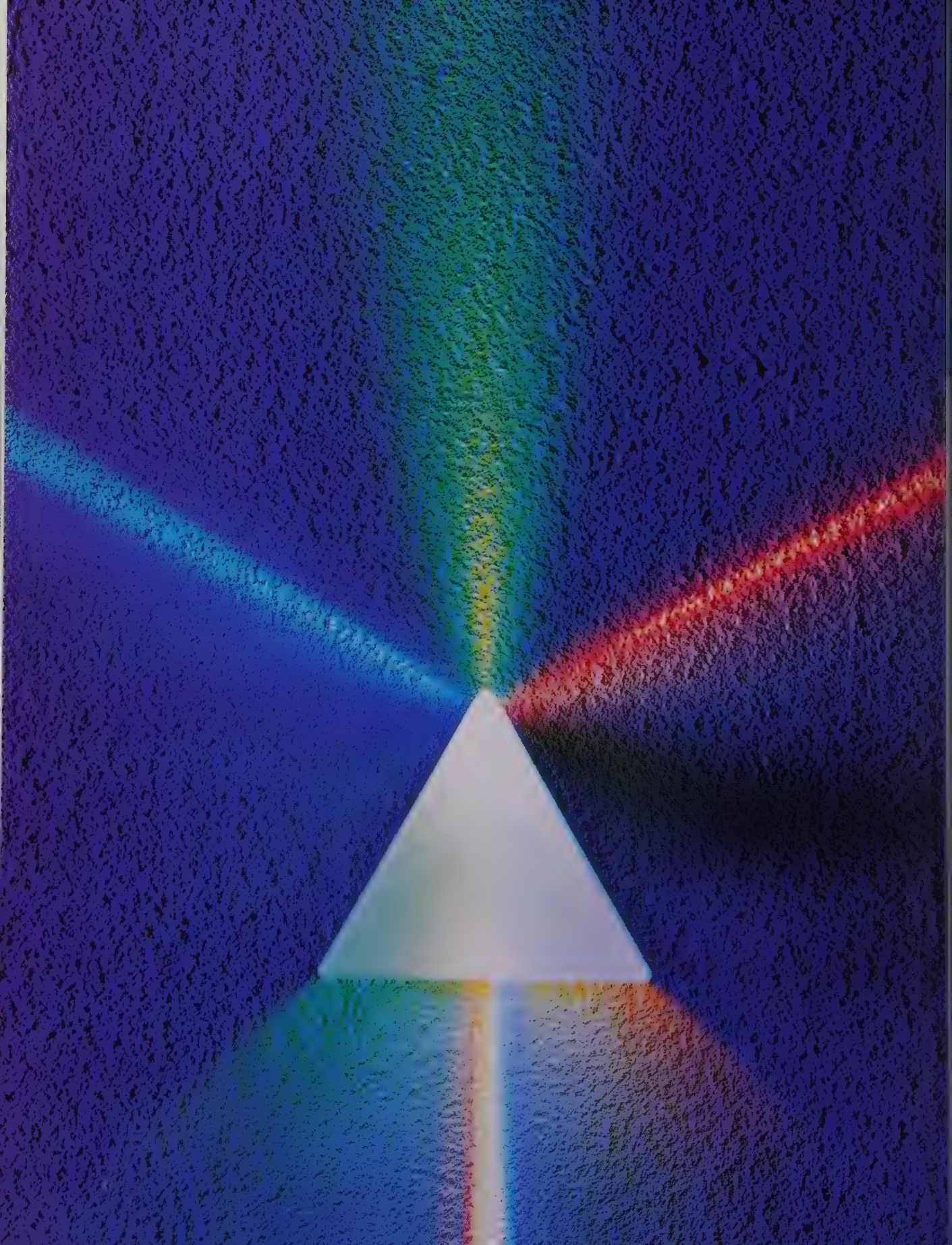
Media Activities

- Read the Chapter 6 Overview on the student CD to review important topics covered in Chapter 6. Then, open the Thermite Reaction Visualization, read the concept, and play the video of this very exothermic reaction.
 - Do the reactants or products in the thermite reaction have a higher potential energy? On average, do the reactants or products have the stronger bonds in this reaction? Explain how the potential energy difference between reactants and products is related to the heat produced in an exothermic reaction.
 - Consider the following endothermic reaction: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g)$. Characterize this reaction in terms of potential energy differences and average bond strength differences between reactant and products. Where does the heat absorbed come from for an endothermic reaction? See Figure 6.3 in the text for a potential energy diagram for this reaction.
 - The heat flow of a system at constant pressure is equal to the enthalpy change. For a chemical reaction, what are the signs of ΔH for an exothermic and for an endothermic reaction? Do Exercises 6.31 and 6.32 in the text to practice predicting signs of ΔH for some processes.
 - The heat absorbed or released is a stoichiometric quantity related to the coefficients of the balanced equation. Do Exercise 6.33 or 6.34 in the text to practice determining quantities of heat released or absorbed in a chemical reaction.
- The Thermite Reaction Visualization on the student CD shows a very exothermic reaction. Calculate ΔH for the thermite reaction using the Standard Enthalpy of Formation Values table. The reactants of the reaction are aluminum and iron(III) oxide; assume that the products are aluminum oxide and iron. For more practice on manipulating standard enthalpy of formation values, try Exercises 6.61, 6.65, and 6.67 in the text.
- Test your understanding of Chapter 6 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

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Atomic Structure and Periodicity

In the past 200 years, a great deal of experimental evidence has accumulated to support the atomic model. This theory has proved to be both extremely useful and physically reasonable. When atoms were first suggested by the Greek philosophers Democritus and Leucippus about 400 B.C., the concept was based mostly on intuition. In fact, for the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms. The first real scientific data were gathered by Lavoisier and others from quantitative measurements of chemical reactions. The results of these stoichiometric experiments led John Dalton to propose the first systematic atomic theory. Dalton's theory, although crude, has stood the test of time extremely well.

Once we came to "believe in" atoms, it was logical to ask: What is the nature of an atom? Does an atom have parts, and if so, what are they? In Chapter 2 we considered some of the experiments most important for shedding light on the nature of the atom. Now we will see how the atomic theory has evolved to its present state.

One of the most striking things about the chemistry of the elements is the periodic repetition of properties. There are several groups of elements that show great similarities in chemical behavior. As we saw in Chapter 2, these similarities led to the development of the periodic table of the elements. In this chapter we will see that the modern theory of atomic structure accounts for periodicity in terms of the electron arrangements in atoms.

However, before we examine atomic structure, we must consider the revolution that took place in physics in the first 30 years of the twentieth century. During that time, experiments were carried out, the results of which could not be explained by the theories of classical physics developed by

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- 7.2 The Nature of Matter**
- 7.3 The Atomic Spectrum of Hydrogen**
- 7.4 The Bohr Model**
- 7.5 The Quantum Mechanical Model of the Atom**
 - The Physical Meaning of a Wave Function
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- 7.7 Orbital Shapes and Energies**
- 7.8 Electron Spin and the Pauli Principle**
- 7.9 Polyelectronic Atoms**
- 7.10 The History of the Periodic Table**
- 7.11 The Aufbau Principle and the Periodic Table**
- 7.12 Periodic Trends in Atomic Properties**
 - Ionization Energy
 - Electron Affinity
 - Atomic Radius
- 7.13 The Properties of a Group: The Alkali Metals**
 - Information Contained in the Periodic Table
 - The Alkali Metals

Isaac Newton and many others who followed him. A radical new theory called *quantum mechanics* was developed to account for the behavior of light and atoms. This “new physics” provides many surprises for humans who are used to the macroscopic world, but it seems to account flawlessly (within the bounds of necessary approximations) for the behavior of matter.

As the first step in our exploration of this revolution in science we will consider the properties of light, more properly called *electromagnetic radiation*.

7.1 Electromagnetic Radiation

One of the ways that energy travels through space is by **electromagnetic radiation**. The light from the sun, the energy used to cook food in a microwave oven, the X rays used by dentists, and the radiant heat from a fireplace are all examples of electromagnetic radiation. Although these forms of radiant energy seem quite different, they all exhibit the same type of wavelike behavior and travel at the speed of light in a vacuum.

Waves have three primary characteristics: wavelength, frequency, and speed. **Wavelength** (symbolized by the lowercase Greek letter lambda, λ) is the *distance between two consecutive peaks or troughs in a wave*, as shown in Fig. 7.1. The **frequency** (symbolized by the lowercase Greek letter nu, ν) is defined as the *number of waves (cycles) per second that pass a given point in space*. Since all types of electromagnetic radiation travel at the speed of light, short-wavelength radiation



Although the waves associated with light are not obvious to the naked eye, ocean waves provide a familiar source of recreation.



Visualization: Electromagnetic Wave

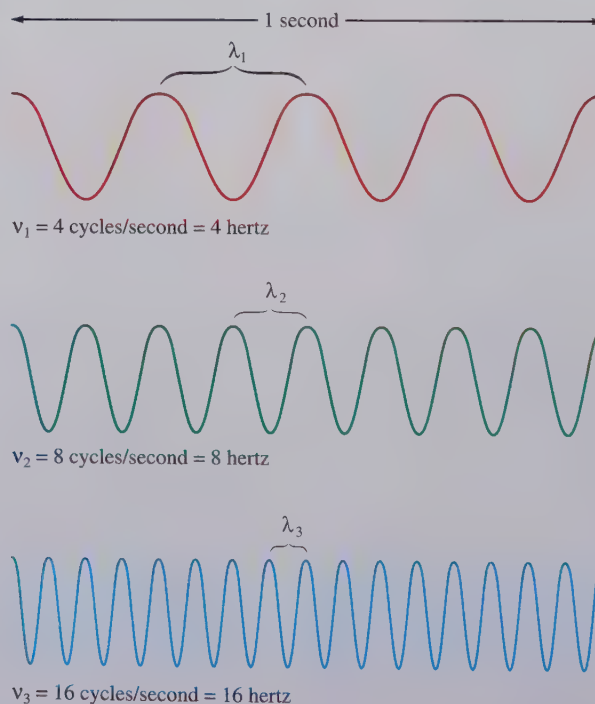


FIGURE 7.1

The nature of waves. Note that the radiation with the shortest wavelength has the highest frequency.

CHEMICAL IMPACT

Flies That Dye

Mediterranean and Mexican fruit flies are formidable pests that have the potential to seriously damage several important fruit crops. Because of this, there have been several widely publicized sprayings of residential areas in southern California with the pesticide malathion to try to control fruit flies. Now there may be a better way to kill fruit flies—with a blend of two common dyes (red dye no. 28 and yellow dye no. 8) long used to color drugs and cosmetics. One of the most interesting things about this new pesticide is that

it is activated by light. After an insect eats the blend of dyes, the molecules absorb light (through the insect's transparent body), which causes them to generate oxidizing agents that attack the proteins and cell membranes in the bug's body. Death occurs within 12 hours.

The sunlight that turns on the dye's toxicity after the fly ingests it also degrades the dye in the environment, making it relatively safe. It appears likely that in the near future the fruit fly will "dye" with little harm to the environment.

Wavelength λ and frequency ν are inversely related.

$$\begin{aligned}c &= \text{speed of light} \\ &= 2.9979 \times 10^8 \text{ m/s}\end{aligned}$$

must have a high frequency. You can see this in Fig. 7.1, where three waves are shown traveling between two points at constant speed. Note that the wave with the shortest wavelength (λ_3) has the highest frequency and the wave with the longest wavelength (λ_1) has the lowest frequency. This implies an inverse relationship between wavelength and frequency, that is, $\lambda \propto 1/\nu$, or

$$\lambda\nu = c$$

where λ is the wavelength in meters, ν is the frequency in cycles per second, and c is the speed of light (2.9979×10^8 m/s). In the SI system, cycles is understood, and the unit per second becomes $1/\text{s}$, or s^{-1} , which is called the *hertz* (abbreviated Hz).

Electromagnetic radiation is classified as shown in Fig. 7.2. Radiation provides an important means of energy transfer. For example, the energy from the sun reaches the earth mainly in the form of visible and ultraviolet radiation, whereas the glowing coals of a fireplace transmit heat energy by infrared radiation. In a microwave oven the water molecules in food absorb microwave radiation, which increases their motions. This energy is then transferred to other types of molecules via collisions, causing an increase in the food's temperature. As we proceed in the study of chemistry, we will consider many of the classes of electromagnetic radiation and the ways in which they affect matter.

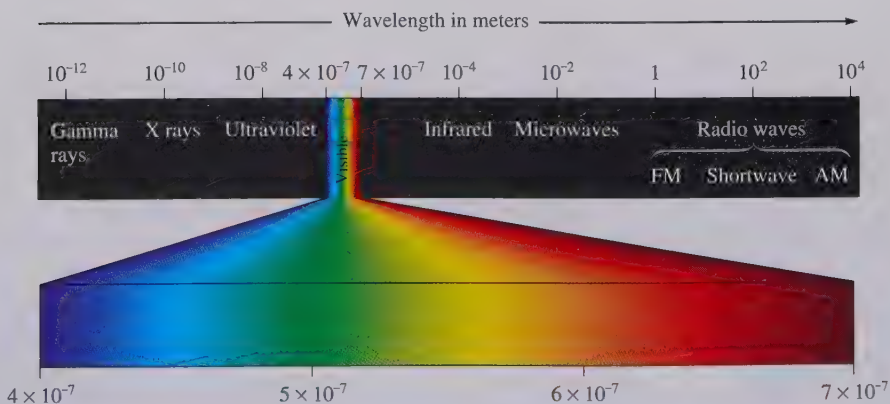


FIGURE 7.2
Classification of electromagnetic radiation.

Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).

SAMPLE EXERCISE 7.1

Frequency of Electromagnetic Radiation

The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $\text{Sr}(\text{NO}_3)_2$ and SrCO_3 are heated. (This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish.) Calculate the frequency of red light of wavelength 6.50×10^2 nm.

SOLUTION

We can convert wavelength to frequency using the equation

$$\lambda\nu = c \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

where $c = 2.9979 \times 10^8$ m/s. In this case $\lambda = 6.50 \times 10^2$ nm. Changing the wavelength to meters, we have

$$6.50 \times 10^2 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.50 \times 10^{-7} \text{ m}$$

and

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.50 \times 10^{-7} \text{ m}} = 4.61 \times 10^{14} \text{ s}^{-1} = 4.61 \times 10^{14} \text{ Hz}$$

See Exercises 7.39 and 7.40.

7.2 The Nature of Matter

It is probably fair to say that at the end of the nineteenth century, physicists were feeling rather smug. Available theories could explain phenomena as diverse as the motions of the planets and the dispersion of visible light by a prism. Rumor has it that students were being discouraged from pursuing physics as a career because it was felt that all the major problems had been solved, or at least described in terms of the current physical theories.

At the end of the nineteenth century, the idea prevailed that matter and energy were distinct. Matter was thought to consist of particles, whereas energy in the form of light (electromagnetic radiation) was described as a wave. Particles were things that had mass and whose position in space could be specified. Waves were described as massless and delocalized; that is, their position in space could not be specified. It also was assumed that there was no intermingling of matter and light. Everything known before 1900 seemed to fit neatly into this view.

At the beginning of the twentieth century, however, certain experimental results suggested that this picture was incorrect. The first important advance came in 1900 from the German physicist Max Planck (1858–1947). Studying the radiation profiles emitted by solid bodies heated to incandescence, Planck found that the results could not be explained in terms of the physics of his day, which held that matter could absorb or emit any quantity of energy. Planck could account for these obser-

When alternating current at 110 volts is applied to a dill pickle, a glowing discharge occurs. The current flowing between the electrodes (forks), which is supported by the Na^+ and Cl^- ions present, apparently causes some sodium atoms to form in an excited state. When these atoms relax to the ground state, they emit visible light at 589 nm, producing the yellow glow reminiscent of sodium vapor lamps.



When a strontium salt is dissolved in methanol (with a little water) and ignited, it gives a brilliant red flame. The red color is produced by emission of light when electrons, excited by the energy of the burning methanol, fall back to their ground states.



CHEMICAL IMPACT

Chemistry That Doesn't Leave You in the Dark

In the animal world, the ability to see at night provides predators with a distinct advantage over their prey. The same advantage can be gained by military forces and law enforcement agencies around the world through the use of recent advances in night vision technology.

All types of night vision equipment are electro-optical devices that amplify existing light. A lens collects light and focuses it on an image intensifier. The image intensifier is based on the photoelectric effect—materials that give off electrons when light is shined on them. Night vision intensifiers use semiconductor-based materials to produce large numbers of electrons for a given input of photons. The emitted electrons are then directed onto a screen covered with compounds that phosphoresce (glow when struck by electrons). While television tubes use various phosphors to produce color pictures, night vision devices use phosphors that appear green, because the human eye can distinguish more shades of green than any other color. The viewing screen shows an image that otherwise would be invisible to the naked eye during nighttime viewing.

Current night vision devices use gallium arsenide (GaAs)-based intensifiers that can amplify input light as much as 50,000 times. These devices are so sensitive they can use starlight to produce an image. It is also now possible to use light (infrared) that cannot be sensed with the human eye to create an image.

This technology, while developed originally for military and law enforcement applications, is now becoming available to the consumer. For example, Cadillac included night vision as an option on its cars for the year 2000. As night-imaging technology improves and costs become less prohibitive, a whole new world is opening up for the technophile—after the sun goes down.



A night vision photo of the midair refueling of a U.S. Air Force plane.

Energy can be gained or lost only in integer multiples of $h\nu$.

Planck's constant = $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$.

variations only by postulating that energy can be gained or lost only in *whole-number multiples* of the quantity $h\nu$, where h is a constant called **Planck's constant**, determined by experiment to have the value $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$. That is, the change in energy for a system ΔE can be represented by the equation

$$\Delta E = nh\nu$$

where n is an integer (1, 2, 3, . . .), h is Planck's constant, and ν is the frequency of the electromagnetic radiation absorbed or emitted.

Planck's result was a real surprise. It had always been assumed that the energy of matter was continuous, which meant that the transfer of any quantity of energy was possible. Now it seemed clear that energy is in fact **quantized** and can occur only in discrete units of size $h\nu$. Each of these small "packets" of energy is called a *quantum*. A system can transfer energy only in whole quanta. Thus energy seems to have particulate properties.

SAMPLE EXERCISE 7.2

The Energy of a Photon

The blue color in fireworks is often achieved by heating copper(I) chloride (CuCl) to about 1200°C . Then the compound emits blue light having a wavelength of 450 nm.

What is the increment of energy (the quantum) that is emitted at 4.50×10^2 nm by CuCl?

SOLUTION

The quantum of energy can be calculated from the equation

$$\Delta E = h\nu$$

The frequency ν for this case can be calculated as follows:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{4.50 \times 10^{-7} \text{ m}} = 6.66 \times 10^{14} \text{ s}^{-1}$$

So

$$\Delta E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(6.66 \times 10^{14} \text{ s}^{-1}) = 4.41 \times 10^{-19} \text{ J}$$

A sample of CuCl emitting light at 450 nm can lose energy only in increments of 4.41×10^{-19} J, the size of the quantum in this case.

See Exercises 7.41 and 7.42.

The next important development in the knowledge of atomic structure came when Albert Einstein (see Fig. 7.3) proposed that electromagnetic radiation is itself quantized. Einstein suggested that electromagnetic radiation can be viewed as a stream of “particles” called **photons**. The energy of each photon is given by the expression

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

where h is Planck’s constant, ν is the frequency of the radiation, and λ is the wavelength of the radiation.

In a related development, Einstein derived the famous equation

$$E = mc^2$$

in his *special theory of relativity* published in 1905. The main significance of this equation is that *energy has mass*. This is more apparent if we rearrange the equation in the following form:

$$m = \frac{E}{c^2}$$

$\leftarrow$ Energy
 $\nwarrow$ Speed of light

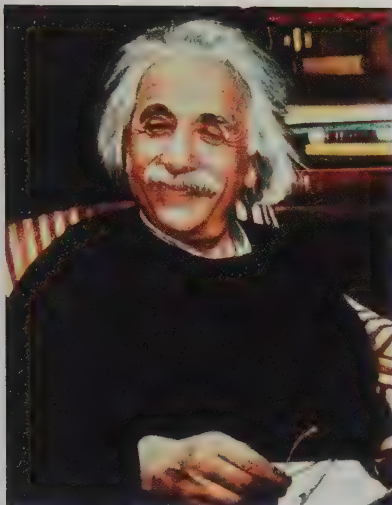
Using this form of the equation, we can calculate the mass associated with a given quantity of energy. For example, we can calculate the *apparent* mass of a photon. For electromagnetic radiation of wavelength λ , the energy of each photon is given by the expression

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Then the apparent mass of a photon of light with wavelength λ is given by

$$m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda c}$$

Note that the apparent mass of a photon depends on its wavelength. The mass of a photon at rest is thought to be zero, although we never observe it at rest.

**FIGURE 7.3**

Albert Einstein (1879–1955) was born in Germany. Nothing in his early development suggested genius; even at the age of 9 he did not speak clearly, and his parents feared that he might be handicapped. When asked what profession Einstein should follow, his school principal replied, “It doesn’t matter; he’ll never make a success of anything.” When he was 10, Einstein entered the Luitpold Gymnasium (high school), which was typical of German schools of that time in being harshly disciplinarian. There he developed a deep suspicion of authority and a skepticism that encouraged him to question and doubt—valuable qualities in a scientist. In 1905, while a patent clerk in Switzerland, Einstein published a paper explaining the photoelectric effect via the quantum theory. For this revolutionary thinking he received a Nobel Prize in 1921. Highly regarded by this time, he worked in Germany until 1933, when Hitler’s persecution of the Jews forced him to come to the United States. He worked at the Institute for Advanced Studies in Princeton, NJ until his death in 1955.

Einstein was undoubtedly the greatest physicist of our age. Even if someone else had derived the theory of relativity, his other work would have ensured his ranking as the second greatest physicist of his time. Our concepts of space and time were radically changed by ideas he first proposed when he was 26 years old. From then until the end of his life, he attempted unsuccessfully to find a single unifying theory that would explain all physical events.



Visualizations: Photoelectric Effect



Light as a wave phenomenon



Light as a stream of photons

FIGURE 7.4

Electromagnetic radiation exhibits wave properties and particulate properties. The energy of each photon of the radiation is related to the wavelength and frequency by the equation $E_{\text{photon}} = h\nu = hc/\lambda$.

Do not confuse ν (frequency) with v (velocity).

Does a photon really have mass? The answer *appears to be* yes. In 1922 American physicist Arthur Compton (1892–1962) performed experiments involving collisions of X rays and electrons that showed that photons do exhibit the apparent mass calculated from the preceding equation. However, it is clear that photons do not have mass in the classical sense. A photon has mass only in a relativistic sense—it has no rest mass.

We can summarize the important conclusions from the work of Planck and Einstein as follows:

Energy is quantized. It can occur only in discrete units called quanta.

Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the **dual nature of light** and is illustrated in Fig. 7.4.

Thus light, which previously was thought to be purely wavelike, was found to have certain characteristics of particulate matter. But is the opposite also true? That is, does matter that is normally assumed to be particulate exhibit wave properties? This question was raised in 1923 by a young French physicist named Louis de Broglie (1892–1987). To see how de Broglie supplied the answer to this question, recall that the relationship between mass and wavelength for electromagnetic radiation is $m = h/\lambda c$. For a particle with velocity v , the corresponding expression is

$$m = \frac{h}{\lambda v}$$

Rearranging to solve for λ , we have

$$\lambda = \frac{h}{mv}$$

This equation, called *de Broglie’s equation*, allows us to calculate the wavelength for a particle, as shown in Sample Exercise 7.3.

SAMPLE EXERCISE 7.3

Calculations of Wavelength

Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.0×10^7 m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

SOLUTION

We use the equation $\lambda = h/mv$, where

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$$

since

$$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$$

For the electron,

$$\lambda_e = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{m}}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^7 \text{ m/s})} = 7.27 \times 10^{-11} \text{ m}$$

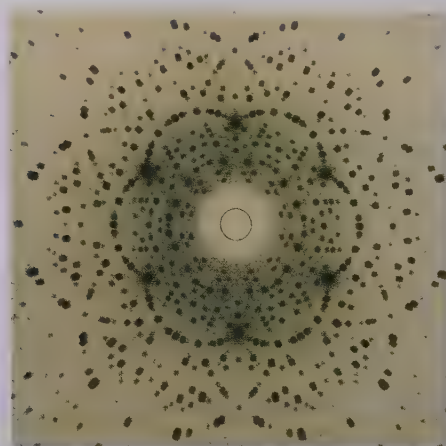
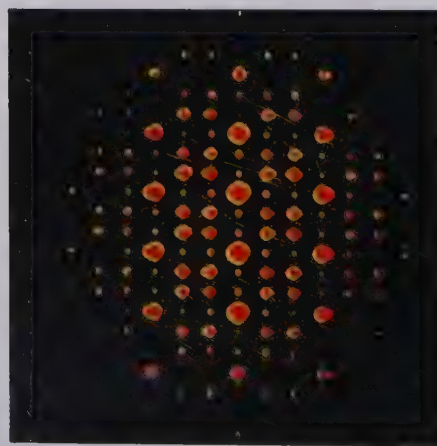
For the ball,

$$\lambda_b = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{m}}{\text{s}}}{(0.10 \text{ kg})(35 \text{ m/s})} = 1.9 \times 10^{-34} \text{ m}$$

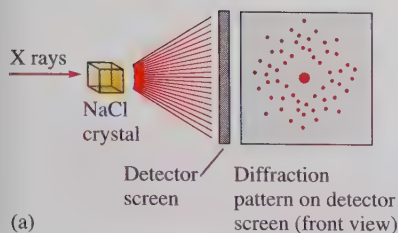
See Exercises 7.47 through 7.50.

Notice from Sample Exercise 7.3 that the wavelength associated with the ball is incredibly short. On the other hand, the wavelength of the electron, although still quite small, happens to be on the same order as the spacing between the atoms in a typical crystal. This is important because, as we will see presently, it provides a means for testing de Broglie's equation.

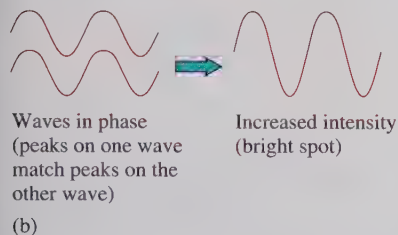
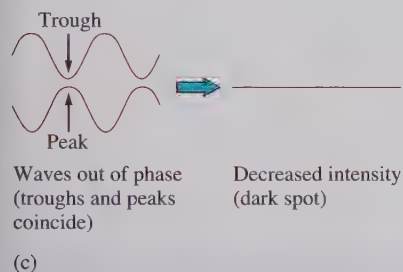
Diffraction results when light is scattered from a regular array of points or lines. You may have noticed the diffraction of light from the ridges and grooves of a compact disc. The colors result because the various wavelengths of visible light are not all scattered in the same way. The colors are “separated,” giving the same effect as light passing through a prism. Just as a regular arrangement of ridges and grooves produces diffraction, so does a regular array of atoms or ions in a crystal, as shown in the photographs below. For example, when X rays are directed onto a



(left) The pattern produced by electron diffraction of a titanium/nickel alloy. (right) Pattern produced by X-ray diffraction of a beryl crystal.

**FIGURE 7.5**

(a) Diffraction occurs when electromagnetic radiation is scattered from a regular array of objects, such as the ions in a crystal of sodium chloride. The large spot in the center is from the main incident beam of X rays. (b) Bright spots in the diffraction pattern result from *constructive interference* of waves. The waves are in phase; that is, their peaks match. (c) Dark areas result from *destructive interference* of waves. The waves are out of phase; the peaks of one wave coincide with the troughs of another wave.

Constructive interference**Destructive interference**

crystal of sodium chloride, with its regular array of Na^+ and Cl^- ions, the scattered radiation produces a **diffraction pattern** of bright spots and dark areas on a photographic plate, as shown in Fig. 7.5(a). This occurs because the scattered light can interfere constructively (the peaks and troughs of the beams are in phase) to produce a bright spot [Fig. 7.5(b)] or destructively (the peaks and troughs are out of phase) to produce a dark area [Fig. 7.5(c)].

A diffraction pattern can only be explained in terms of waves. Thus this phenomenon provides a test for the postulate that particles such as electrons have wavelengths. As we saw in Sample Exercise 7.3, an electron with a velocity of 10^7 m/s (easily achieved by acceleration of the electron in an electric field) has a wavelength of about 10^{-10} m, which is roughly the distance between the ions in a crystal such as sodium chloride. This is important because diffraction occurs most efficiently when the spacing between the scattering points is about the same as the wavelength of the wave being diffracted. Thus, if electrons really do have an associated wavelength, a crystal should diffract electrons. An experiment to test this idea was carried out in 1927 by C. J. Davisson and L. H. Germer at Bell Laboratories. When they directed a beam of electrons at a nickel crystal, they observed a diffraction pattern similar to that seen from the diffraction of X rays. This result verified de Broglie's relationship, at least for electrons. Larger chunks of matter, such as balls, have such small wavelengths (see Sample Exercise 7.3) that they are impossible to verify experimentally. However, we believe that all matter obeys de Broglie's equation.

Now we have come full circle. Electromagnetic radiation, which at the turn of the twentieth century was thought to be a pure waveform, was found to possess particulate properties. Conversely, electrons, which were thought to be particles, were found to have a wavelength associated with them. The significance of these results is that matter and energy are not distinct. Energy is really a form of matter, and all matter shows the same types of properties. That is, *all matter exhibits both particulate and wave properties*. Large pieces of matter, such as baseballs, exhibit predominantly particulate properties. The associated wavelength is so small that it is not observed. Very small "bits of matter," such as photons, while showing some particulate properties, exhibit predominantly wave properties. Pieces of matter with intermediate mass, such as electrons, show clearly both the particulate and wave properties of matter.

7.3 The Atomic Spectrum of Hydrogen

As we saw in Chapter 2, key information about the atom came from several experiments carried out in the early twentieth century, in particular Thomson's discovery of the electron and Rutherford's discovery of the nucleus. Another important experiment was the study of the emission of light by excited hydrogen atoms. When a sample of hydrogen gas receives a high-energy spark, the H_2 molecules absorb energy, and some of the H—H bonds are broken. The resulting hydrogen atoms are *excited*;

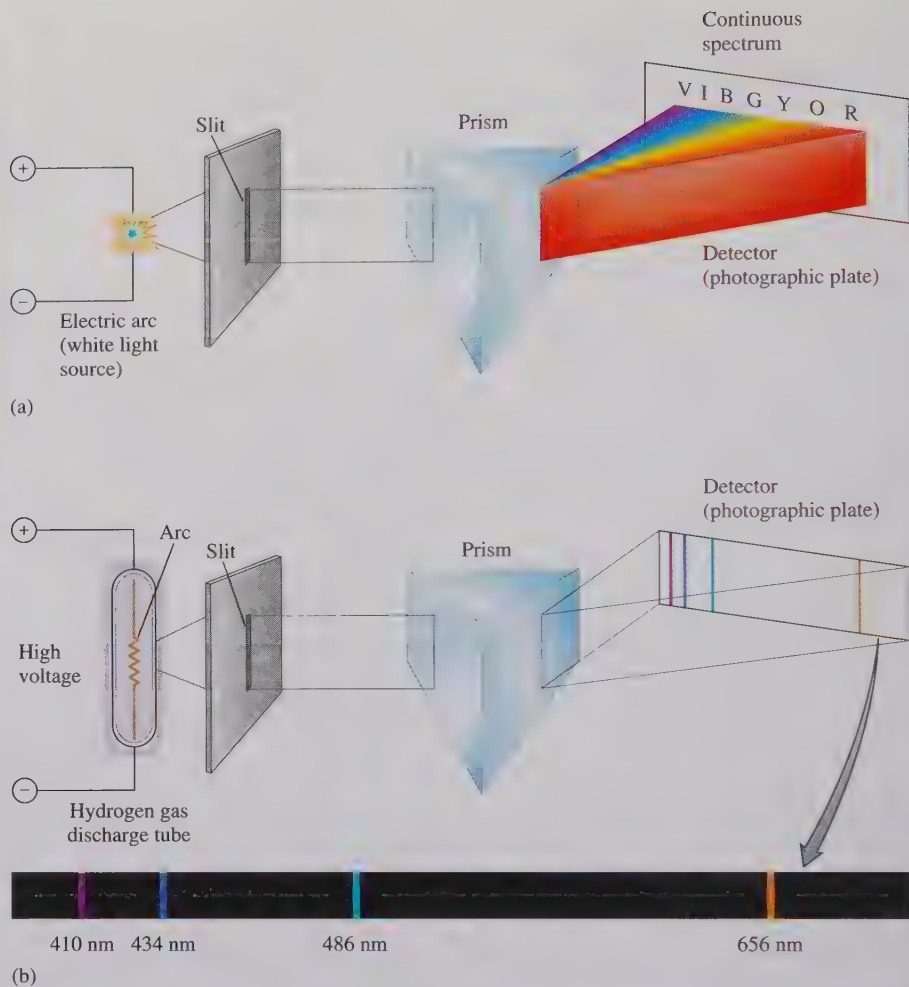


A beautiful rainbow.

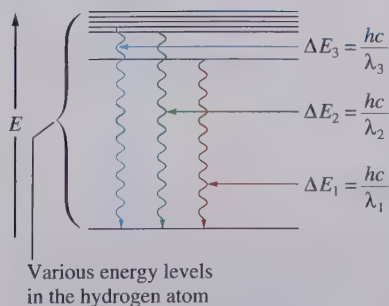
FIGURE 7.6

(a) A continuous spectrum containing all wavelengths of visible light (indicated by the initial letters of the colors of the rainbow). (b) The hydrogen line spectrum contains only a few discrete wavelengths.

Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).



Visualizations: Refraction of White Light and H_2 Line Spectrum

**FIGURE 7.7**

A change between two discrete energy levels emits a photon of light.

that is, they contain excess energy, which they release by emitting light of various wavelengths to produce what is called the *emission spectrum* of the hydrogen atom.

To understand the significance of the hydrogen emission spectrum, we must first describe the **continuous spectrum** that results when white light is passed through a prism, as shown in Fig. 7.6(a). This spectrum, like the rainbow produced when sunlight is dispersed by raindrops, contains *all* the wavelengths of visible light. In contrast, when the hydrogen emission spectrum in the visible region is passed through a prism, as shown in Fig. 7.6(b), we see only a few lines, each of which corresponds to a discrete wavelength. The hydrogen emission spectrum is called a **line spectrum**.

What is the significance of the line spectrum of hydrogen? It indicates that *only certain energies are allowed for the electron in the hydrogen atom*. In other words, the energy of the electron in the hydrogen atom is *quantized*. This observation ties in perfectly with the postulates of Max Planck discussed in Section 7.2. Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light, as shown in Fig. 7.7. For example, a given change in energy from a high to a lower level would give a wavelength of light that can be calculated from Planck's equation:

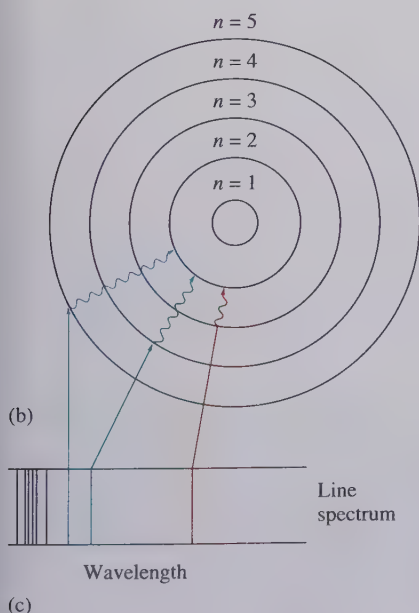
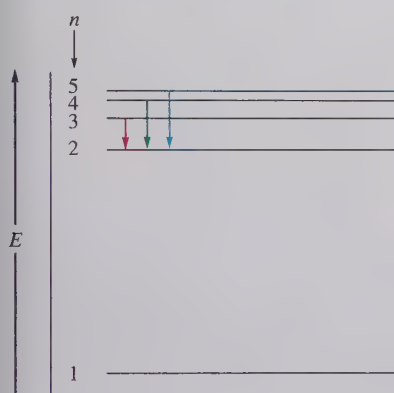
$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Change in energy
Frequency of light emitted
Wavelength of light emitted

The discrete line spectrum of hydrogen shows that only certain energies are possible; that is, the electron energy levels are quantized. In contrast, if any energy level were allowed, the emission spectrum would be continuous.

7.4 The Bohr Model

The J in Equation (7.1) stands for joules.



In 1913, a Danish physicist named Niels Bohr (1885–1962), aware of the experimental results we have just discussed, developed a **quantum model** for the hydrogen atom. Bohr proposed that the *electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits*. He calculated the radii for these allowed orbits by using the theories of classical physics and by making some new assumptions.

From classical physics Bohr knew that a particle in motion tends to move in a straight line and can be made to travel in a circle only by application of a force toward the center of the circle. Thus Bohr reasoned that the tendency of the revolving electron to fly off the atom must be just balanced by its attraction for the positively charged nucleus. But classical physics also decreed that a charged particle under acceleration should radiate energy. Since an electron revolving around the nucleus constantly changes its direction, it is constantly accelerating. Therefore, the electron should emit light and lose energy—and thus be drawn into the nucleus. This, of course, does not correlate with the existence of stable atoms.

Clearly, an atomic model based solely on the theories of classical physics was untenable. Bohr also knew that the correct model had to account for the experimental spectrum of hydrogen, which showed that only certain electron energies were allowed. The experimental data were absolutely clear on this point. Bohr found that his model would fit the experimental results if he assumed that the angular momentum of the electron (angular momentum equals the product of mass, velocity, and orbital radius) could occur only in certain increments. It was not clear why this should be true, but with this assumption, Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum. The model is represented pictorially in Fig. 7.8.

Although we will not show the derivation here, the most important equation to come from Bohr's model is the expression for the *energy levels available to the electron in the hydrogen atom*:

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right) \quad (7.1)$$

in which n is an integer (the larger the value of n , the larger is the orbit radius) and Z is the nuclear charge. Using Equation (7.1), Bohr was able to calculate hydrogen atom energy levels that exactly matched the values obtained by experiment.

FIGURE 7.8

Electronic transitions in the Bohr model for the hydrogen atom. (a) An energy-level diagram for electronic transitions. (b) An orbit-transition diagram, which accounts for the experimental spectrum. (Note that the orbits shown are schematic. They are not drawn to scale.) (c) The resulting line spectrum on a photographic plate. Note that the lines in the visible region of the spectrum correspond to transitions from higher levels to the $n = 2$ level.



Niels Hendrik David Bohr (1885–1962) as a boy lived in the shadow of his younger brother Harald, who played on the 1908 Danish Olympic Soccer Team and later became a distinguished mathematician. In school, Bohr received his poorest marks in composition and struggled with writing during his entire life. In fact, he wrote so poorly that he was forced to dictate his Ph.D. thesis to his mother. Nevertheless, Bohr was a brilliant physicist. After receiving his Ph.D. in Denmark, he constructed a quantum model for the hydrogen atom by the time he was 27. Even though his model later proved to be incorrect, Bohr remained a central figure in the drive to understand the atom. He was awarded the Nobel Prize in physics in 1922.

The negative sign in Equation (7.1) simply means that the energy of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance ($n = \infty$) from the nucleus, where there is no interaction and the energy is zero:

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{\infty} \right) = 0$$

The energy of the electron in any orbit is negative relative to this reference state.

Equation (7.1) can be used to calculate the change in energy of an electron when the electron changes orbits. For example, suppose an electron in level $n = 6$ of an excited hydrogen atom falls back to level $n = 1$ as the hydrogen atom returns to its lowest possible energy state, its **ground state**. We use Equation (7.1) with $Z = 1$, since the hydrogen nucleus contains a single proton. The energies corresponding to the two states are as follows:

$$\text{For } n = 6: \quad E_6 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{6^2} \right) = -6.050 \times 10^{-20} \text{ J}$$

$$\text{For } n = 1: \quad E_1 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

Note that for $n = 1$ the electron has a more negative energy than it does for $n = 6$, which means that the electron is more tightly bound in the smallest allowed orbit.

The change in energy ΔE when the electron falls from $n = 6$ to $n = 1$ is

$$\begin{aligned} \Delta E &= \text{energy of final state} - \text{energy of initial state} \\ &= E_1 - E_6 = (-2.178 \times 10^{-18} \text{ J}) - (-6.050 \times 10^{-20} \text{ J}) \\ &= -2.117 \times 10^{-18} \text{ J} \end{aligned}$$

The negative sign for the *change* in energy indicates that the atom has *lost* energy and is now in a more stable state. The energy is carried away from the atom by the production (emission) of a photon.

The wavelength of the emitted photon can be calculated from the equation

$$\Delta E = h \left(\frac{c}{\lambda} \right) \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

where ΔE represents the change in energy of the atom, which equals the energy of the emitted photon. We have

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{2.117 \times 10^{-18} \text{ J}} = 9.383 \times 10^{-8} \text{ m}$$

Note that for this calculation the absolute value of ΔE is used (we have not included the negative sign). In this case we indicate the direction of energy flow by saying that a photon of wavelength $9.383 \times 10^{-8} \text{ m}$ has been *emitted* from the hydrogen atom. Simply plugging the negative value of ΔE into the equation would produce a negative value for λ , which is physically meaningless.

SAMPLE EXERCISE 7.4

Energy Quantization in Hydrogen

Calculate the energy required to excite the hydrogen electron from level $n = 1$ to level $n = 2$. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.*

*After this exercise we will no longer show cancellation marks. However, the same process for canceling units applies throughout this text.

SOLUTION

Using Equation (7.1) with $Z = 1$, we have

$$E_1 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

$$E_2 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{2^2} \right) = -5.445 \times 10^{-19} \text{ J}$$

$$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-19} \text{ J}) - (-2.178 \times 10^{-18} \text{ J}) = 1.633 \times 10^{-18} \text{ J}$$

The positive value for ΔE indicates that the system has gained energy. The wavelength of light that must be *absorbed* to produce this change is

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{1.633 \times 10^{-18} \text{ J}} \\ &= 1.216 \times 10^{-7} \text{ m} \end{aligned}$$

Note from Fig. 7.2 that the light required to produce the transition from the $n = 1$ to $n = 2$ level in hydrogen lies in the ultraviolet region.

See Exercises 7.51 and 7.52.

At this time we must emphasize two important points about the Bohr model:

1. The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
2. As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (corresponding to the electron being at infinite distance from the nucleus). As the electron is brought closer to the nucleus, energy is released from the system.

Using Equation (7.1), we can derive a general equation for the electron moving from one level (n_{initial}) to another level (n_{final}):

$$\begin{aligned} \Delta E &= \text{energy of level } n_{\text{final}} - \text{energy of level } n_{\text{initial}} \\ &= E_{\text{final}} - E_{\text{initial}} \\ &= (-2.178 \times 10^{-18} \text{ J}) \left(\frac{1^2}{n_{\text{final}}^2} \right) - (-2.178 \times 10^{-18} \text{ J}) \left(\frac{1^2}{n_{\text{initial}}^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \end{aligned} \quad (7.2)$$

Equation (7.2) can be used to calculate the energy change between *any* two energy levels in a hydrogen atom, as shown in Sample Exercise 7.5.

SAMPLE EXERCISE 7.5

Electron Energies

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

SOLUTION

Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from $n_{\text{initial}} = 1$ to $n_{\text{final}} = \infty$. Thus

CHEMICAL IMPACT

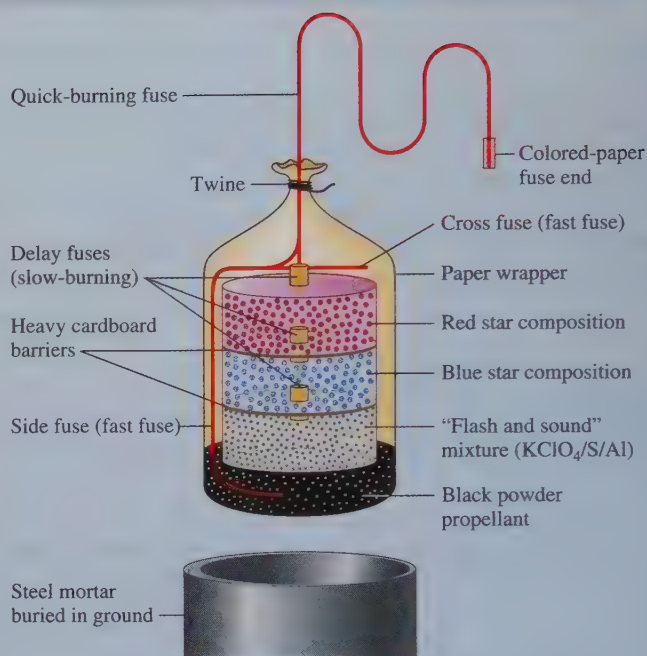
Fireworks

The art of using mixtures of chemicals to produce explosives is an ancient one. Black powder—a mixture of potassium nitrate, charcoal, and sulfur—was being used in China well before 1000 A.D. and has been used subsequently through the centuries in military explosives, in construction blasting, and for fireworks. The Du Pont Company, now a major chemical manufacturer, started out as a manufacturer of black powder. In fact, the founder, Eleuthère du Pont, learned the manufacturing technique from none other than Lavoisier.

Before the nineteenth century, fireworks were confined mainly to rockets and loud bangs. Orange and yellow colors came from the presence of charcoal and iron filings. However, with the great advances in chemistry in the nineteenth century, new compounds found their way into fireworks. Salts of copper, strontium, and barium added brilliant colors. Magnesium and aluminum metals gave a dazzling white light. Fireworks, in fact, have changed very little since then.

How do fireworks produce their brilliant colors and loud bangs? Actually, only a handful of different chemicals are responsible for most of the spectacular effects. To produce the noise and flashes, an oxidizer (an oxidizing agent) and a fuel (a reducing agent) are used. A common mixture involves potassium perchlorate (KClO_4) as the oxidizer and aluminum and sulfur as the fuel. The perchlorate oxidizes the fuel in a very exothermic reaction, which produces a brilliant flash, due to the aluminum, and a loud report from the rapidly expanding gases produced. For a color effect, an element with a colored emission spectrum is included. Recall that the electrons in atoms can be raised to higher-energy orbitals when the atoms absorb energy. The excited atoms can then release this excess energy by emitting light of specific wavelengths, often in the visible region. In fireworks, the energy to excite the electrons comes from the reaction between the oxidizer and fuel.

Yellow colors in fireworks are due to the 589-nm emission of sodium ions. Red colors come from strontium salts emitting at 606 nm and from 636 to 688 nm. This red color is familiar from highway safety flares. Barium salts give a green color in fireworks, due to a series of emission lines between 505 and 535 nm. A really good blue color, however, is hard to obtain. Copper salts give a blue color, emitting in the 420- to 460-nm region. But difficulties occur because the oxidizing agent, potassium chlorate (KClO_3), reacts with copper salts to form copper chlorate, a highly explosive compound that is dangerous to store. (The use of KClO_3 in fire-



A typical aerial shell used in fireworks displays. Time-delayed fuses cause a shell to explode in stages. In this case a red starburst occurs first, followed by a blue starburst, and finally a flash and loud report.

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works has been largely abandoned because of its explosive hazards.) Paris green, a copper salt containing arsenic, was once used extensively but is now considered to be too toxic.

In recent years the colors produced by fireworks have become more intense because of the formation of metal chlorides during the burning process. These gaseous metal chloride molecules produce colors much more brilliant than do the metal atoms by themselves. For example, strontium chloride produces a much brighter red than do strontium atoms. Thus, chlorine-donating compounds are now included in many fireworks shells.

A typical aerial shell is shown in the diagram. The shell is launched from a mortar (a steel cylinder) using black powder as the propellant. Time-delayed fuses are used to fire the shell in stages. A list of chemicals commonly used in fireworks is given in the table.

Although you might think that the chemistry of fireworks is simple, the achievement of the vivid white flashes and the



Fireworks in Washington, D.C.

brilliant colors requires complex combinations of chemicals. For example, because the white flashes produce high flame temperatures, the colors tend to wash out. Thus oxidizers such as KClO_4 are commonly used with fuels that produce relatively low flame temperatures. An added difficulty, however, is that perchlorates are very sensitive to accidental ignition and are therefore quite hazardous. Another problem arises from the use of sodium salts. Because sodium produces an extremely bright yellow emission, sodium salts cannot be used when other colors are desired. Carbon-based fuels also give a yellow flame that masks other colors, and this limits the use of organic compounds as fuels. You can see that the manufacture of fireworks that produce the desired effects and are also safe to handle requires careful selection of chemicals. And, of course, there is still the dream of a deep blue flame.

Chemicals Commonly Used in the Manufacture of Fireworks

Oxidizers	Fuels	Special Effects
Potassium nitrate	Aluminum	Red flame: strontium nitrate, strontium carbonate
Potassium chlorate	Magnesium	Green flame: barium nitrate, barium chlorate
Potassium perchlorate	Titanium	Blue flame: copper carbonate, copper sulfate, copper oxide
Ammonium perchlorate	Charcoal	Yellow flame: sodium oxalate, cryolite (Na_3AlF_6)
Barium nitrate	Sulfur	White flame: magnesium, aluminum
Barium chlorate	Antimony sulfide	Gold sparks: iron filings, charcoal
Strontium nitrate	Dextrin	White sparks: aluminum, magnesium, aluminum–magnesium alloy, titanium
	Red gum	Whistle effect: potassium benzoate or sodium salicylate
	Polyvinyl chloride	White smoke: mixture of potassium nitrate and sulfur
		Colored smoke: mixture of potassium chlorate, sulfur, and organic dye



Visualization: Flame Tests

$$\begin{aligned}
 \Delta E &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \\
 &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{\infty} - \frac{1}{1^2} \right) \\
 &= -2.178 \times 10^{-18} \text{ J}(0 - 1) = 2.178 \times 10^{-18} \text{ J}
 \end{aligned}$$

The energy required to remove the electron from a hydrogen atom in its ground state is $2.178 \times 10^{-18} \text{ J}$.

See Exercise 7.56.

Although Bohr's model fits the energy levels for hydrogen, it is a fundamentally incorrect model for the hydrogen atom.

At first Bohr's model appeared to be very promising. The energy levels calculated by Bohr closely agreed with the values obtained from the hydrogen emission spectrum. However, when Bohr's model was applied to atoms other than hydrogen, it did not work at all. Although some attempts were made to adapt the model using elliptical orbits, it was concluded that Bohr's model is fundamentally incorrect. The model is, however, very important historically, because it showed that the observed quantization of energy in atoms could be explained by making rather simple assumptions. Bohr's model paved the way for later theories. It is important to realize, however, that the current theory of atomic structure is in no way derived from the Bohr model. Electrons do *not* move around the nucleus in circular orbits, as we shall see later in this chapter.

7.5 The Quantum Mechanical Model of the Atom

By the mid-1920s it had become apparent that the Bohr model could not be made to work. A totally new approach was needed. Three physicists were at the forefront of this effort: Werner Heisenberg (1901–1976), Louis de Broglie (1892–1987), and Erwin Schrödinger (1887–1961). The approach they developed became known as *wave mechanics* or, more commonly, *quantum mechanics*. As we have already seen, de Broglie originated the idea that the electron, previously considered to be a particle, also shows wave properties. Pursuing this line of reasoning, Schrödinger, an Austrian physicist, decided to attack the problem of atomic structure by giving emphasis to the wave properties of the electron. To Schrödinger and de Broglie, the electron bound to the nucleus seemed similar to a **standing wave**, and they began research on a wave mechanical description of the atom.

The most familiar example of standing waves occurs in association with musical instruments such as guitars or violins, where a string attached at both ends vibrates to produce a musical tone. The waves are described as “standing” because they are stationary; the waves do not travel along the length of the string. The motions of the string can be explained as a combination of simple waves of the type shown in Fig. 7.9. The dots in this figure indicate the nodes, or points of zero lateral (sideways) displacement, for a given wave. Note that there are limitations on the allowed wavelengths of the standing wave. Each end of the string is fixed, so there is always a node at each end. This means that there must be a whole number of *half* wavelengths in any of the allowed motions of the string (see Fig. 7.9). Standing waves can be illustrated using the wave generator shown in the photo below.

A similar situation results when the electron in the hydrogen atom is imagined to be a standing wave. As shown in Fig. 7.10, only certain circular orbits have a circumference into which a whole number of wavelengths of the standing electron wave will “fit.” All other orbits would produce destructive interference of the standing electron wave and are not allowed. This seemed like a possible explanation for the ob-

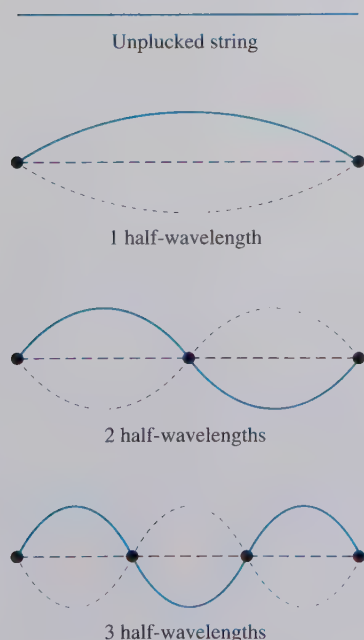
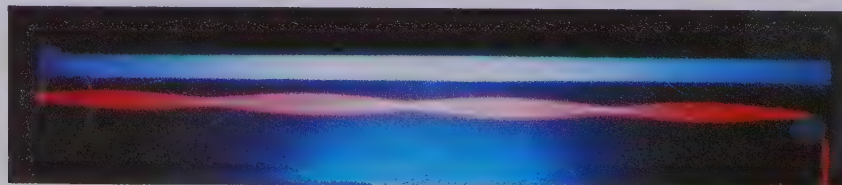
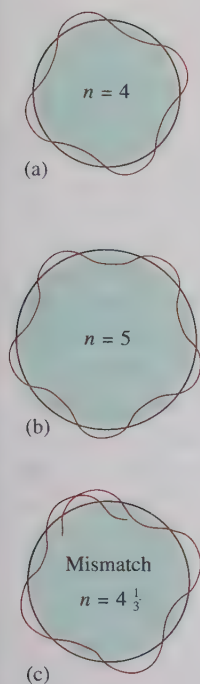


FIGURE 7.9

The standing waves caused by the vibration of a guitar string fastened at both ends. Each dot represents a node (a point of zero displacement).

Wave-generating apparatus.



**FIGURE 7.10**

The hydrogen electron visualized as a standing wave around the nucleus. The circumference of a particular circular orbit would have to correspond to a whole number of wavelengths, as shown in (a) and (b), or else destructive interference occurs, as shown in (c). This is consistent with the fact that only certain electron energies are allowed; the atom is quantized. (Although this idea encouraged scientists to use a wave theory, it does not mean that the electron really travels in circular orbits.)

served quantization of the hydrogen atom, so Schrödinger worked out a model for the hydrogen atom in which the electron was assumed to behave as a standing wave.

It is important to recognize that Schrödinger could not be sure that this idea would work. The test had to be whether or not the model would correctly fit the experimental data on hydrogen and other atoms. The physical principles for describing standing waves were well known in 1925 when Schrödinger decided to treat the electron in this way. His mathematical treatment is too complicated to be detailed here. However, the form of Schrödinger's equation is

$$\hat{H}\psi = E\psi$$

where ψ , called the **wave function**, is a function of the coordinates (x , y , and z) of the electron's position in three-dimensional space and $\hat{H}$ represents a set of mathematical instructions called an *operator*. In this case, the operator contains mathematical terms that produce the total energy of the atom when they are applied to the wave function. E represents the total energy of the atom (the sum of the potential energy due to the attraction between the proton and electron and the kinetic energy of the moving electron). When this equation is analyzed, many solutions are found. Each solution consists of a wave function ψ that is characterized by a particular value of E . A specific wave function is often called an **orbital**.

To illustrate the most important ideas of the **quantum (wave) mechanical model** of the atom, we will first concentrate on the wave function corresponding to the lowest energy for the hydrogen atom. This wave function is called the **1s orbital**. The first point of interest is to explore the meaning of the word *orbital*. As we will see, this is not a trivial matter. One thing is clear: An orbital is *not* a Bohr orbit. The electron in the hydrogen 1s orbital is not moving around the nucleus in a circular orbit. How, then, is the electron moving? The answer is quite surprising: *We do not know*. The wave function gives us no information about the detailed pathway of the electron. This is somewhat disturbing. When we solve problems involving the motions of particles in the macroscopic world, we are able to predict their pathways. For example, when two billiard balls with known velocities collide, we can predict their motions after the collision. However, we cannot predict the electron's motion from the 1s orbital function. Does this mean that the theory is wrong? Not necessarily: We have already learned that an electron does not behave much like a billiard ball, so we must examine the situation closely before we discard the theory.

To help us understand the nature of an orbital, we need to consider a principle discovered by Werner Heisenberg, one of the primary developers of quantum mechanics. Heisenberg's mathematical analysis led him to a surprising conclusion: *There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time*. This is a statement of the **Heisenberg uncertainty principle**. Stated mathematically, the uncertainty principle is

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

where Δx is the uncertainty in a particle's position, $\Delta(mv)$ is the uncertainty in a particle's momentum, and h is Planck's constant. Thus the minimum uncertainty in the product $\Delta x \cdot \Delta(mv)$ is $h/4\pi$. What this equation really says is that the more accurately we know a particle's position, the less accurately we can know its momentum, and vice versa. This limitation is so small for large particles such as baseballs or billiard balls that it is unnoticed. However, for a small particle such as the electron, the limitation becomes quite important. Applied to the electron, the uncertainty

principle implies that we cannot know the exact motion of the electron as it moves around the nucleus. It is therefore not appropriate to assume that the electron is moving around the nucleus in a well-defined orbit, as in the Bohr model.

The Physical Meaning of a Wave Function

Given the limitations indicated by the uncertainty principle, what then is the physical meaning of a wave function for an electron? That is, what is an atomic orbital? Although the wave function itself has no easily visualized meaning, the square of the function does have a definite physical significance. *The square of the function indicates the probability of finding an electron near a particular point in space.* For example, suppose we have two positions in space, one defined by the coordinates x_1 , y_1 , and z_1 and the other by the coordinates x_2 , y_2 , and z_2 . The relative probability of finding the electron at positions 1 and 2 is given by substituting the values of x , y , and z for the two positions into the wave function, squaring the function value, and computing the following ratio:

$$\frac{[\psi(x_1, y_1, z_1)]^2}{[\psi(x_2, y_2, z_2)]^2} = \frac{N_1}{N_2}$$

The quotient N_1/N_2 is the ratio of the probabilities of finding the electron at positions 1 and 2. For example, if the value of the ratio N_1/N_2 is 100, the electron is 100 times more likely to be found at position 1 than at position 2. The model gives no information concerning when the electron will be at either position or how it moves between the positions. This vagueness is consistent with the concept of the Heisenberg uncertainty principle.

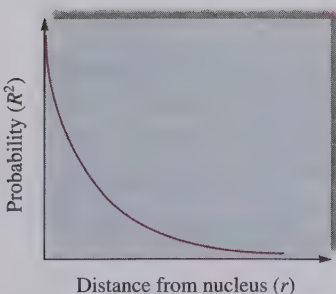
The square of the wave function is most conveniently represented as a **probability distribution**, in which the intensity of color is used to indicate the probability value near a given point in space. The probability distribution for the hydrogen 1s wave function (orbital) is shown in Fig. 7.11(a). The best way to think about this diagram is as a three-dimensional time exposure with the electron as a tiny moving light. The more times the electron visits a particular point, the darker the negative becomes. Thus the darkness of a point indicates the probability of finding an electron at that position. This diagram is also known as an *electron density map*; *electron density* and *electron probability* mean the same thing. When a chemist uses the term *atomic orbital*, he or she is probably picturing an electron density map of this type.

Another way of representing the electron probability distribution for the 1s wave function is to calculate the probability at points along a line drawn outward in any direction from the nucleus. The result is shown in Fig. 7.11(b). Note that the probability of finding the electron at a particular position is greatest close to the nucleus and it drops off rapidly as the distance from the nucleus increases. We are also interested in knowing the *total* probability of finding the electron in the hydrogen atom at a particular *distance* from the nucleus. Imagine that the space around the hydrogen nucleus is made up of a series of thin spherical shells (rather like layers in an onion), as shown in Fig. 7.12(a). When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, the plot in Fig. 7.12(b) is obtained. This graph is called the **radial probability distribution**.

The maximum in the curve occurs because of two opposing effects. The probability of finding an electron at a particular position is greatest near the nucleus, but the volume of the spherical shell increases with distance from the nucleus. Therefore, as we move away from the nucleus, the probability of finding the electron at

Probability is the likelihood, or odds, that something will occur.

(a)



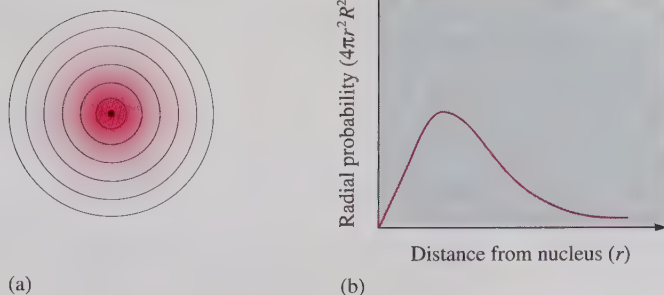
(b)

FIGURE 7.11

(a) The probability distribution for the hydrogen 1s orbital in three-dimensional space. (b) The probability of finding the electron at points along a line drawn from the nucleus outward in any direction for the hydrogen 1s orbital.

FIGURE 7.12

(a) Cross section of the hydrogen 1s orbital probability distribution divided into successive thin spherical shells. (b) The radial probability distribution. A plot of the total probability of finding the electron in each thin spherical shell as a function of distance from the nucleus.



$1 \text{ \AA} = 10^{-10} \text{ m}$; the angstrom is most often used as the unit for atomic radius because of its convenient size. Another convenient unit is the picometer:

$$1 \text{ pm} = 10^{-12} \text{ m}$$

a given position decreases, but we are summing more positions. Thus the total probability increases to a certain radius and then decreases as the electron probability at each position becomes very small. For the hydrogen 1s orbital, the maximum radial probability (the distance at which the electron is most likely to be found) occurs at a distance of $5.29 \times 10^{-2} \text{ nm}$ or $0.529 \text{ \AA}$ from the nucleus. Interestingly, this is exactly the radius of the innermost orbit in the Bohr model. Note that in Bohr's model the electron is assumed to have a circular path and so is *always* found at this distance. In the quantum mechanical model, the specific electron motions are unknown, and this is the *most probable* distance at which the electron is found.

One more characteristic of the hydrogen 1s orbital that we must consider is its size. As we can see from Fig. 7.11, the size of this orbital cannot be defined precisely, since the probability never becomes zero (although it drops to an extremely small value at large values of r). So, in fact, the hydrogen 1s orbital has no distinct size. However, it is useful to have a definition of relative orbital size. *The definition most often used by chemists to describe the size of the hydrogen 1s orbital is the radius of the sphere that encloses 90% of the total electron probability.* That is, 90% of the time the electron is inside this sphere.

So far we have described only the lowest-energy wave function in the hydrogen atom, the 1s orbital. Hydrogen has many other orbitals, which we will describe in the next section. However, before we proceed, we should summarize what we have said about the meaning of an atomic orbital. An orbital is difficult to define precisely at an introductory level. Technically, an orbital is a wave function. However, it is usually most helpful to picture an orbital as a three-dimensional electron density map. That is, an electron “in” a particular atomic orbital is assumed to exhibit the electron probability indicated by the orbital map.

7.6 Quantum Numbers

When we solve the Schrödinger equation for the hydrogen atom, we find many wave functions (orbitals) that satisfy it. Each of these orbitals is characterized by a series of numbers called **quantum numbers**, which describe various properties of the orbital:

The **principal quantum number** (n) has integral values: 1, 2, 3, ... The principal quantum number is related to the size and energy of the orbital. As n increases, the orbital becomes larger and the electron spends more time farther from the nucleus. An increase in n also means higher energy, because the electron is less tightly bound to the nucleus, and the energy is less negative.

TABLE 7.1 The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

Value of ℓ	0	1	2	3	4
Letter Used	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>

Number of Orbitals per Subshell

$$\begin{aligned}s &= 1 \\p &= 3 \\d &= 5 \\f &= 7 \\g &= 9\end{aligned}$$

TABLE 7.2 Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

<i>n</i>	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1 <i>s</i>	0	1
2	0	2 <i>s</i>	0	1
	1	2 <i>p</i>	-1, 0, +1	3
3	0	3 <i>s</i>	0	1
	1	3 <i>p</i>	-1, 0, 1	3
	2	3 <i>d</i>	-2, -1, 0, 1, 2	5
4	0	4 <i>s</i>	0	1
	1	4 <i>p</i>	-1, 0, 1	3
	2	4 <i>d</i>	-2, -1, 0, 1, 2	5
	3	4 <i>f</i>	-3, -2, -1, 0, 1, 2, 3	7

The **angular momentum quantum number** (ℓ) has integral values from 0 to $n - 1$ for each value of n . This quantum number is related to the shape of atomic orbitals. The value of ℓ for a particular orbital is commonly assigned a letter: $\ell = 0$ is called *s*; $\ell = 1$ is called *p*; $\ell = 2$ is called *d*; $\ell = 3$ is called *f*. This system arises from early spectral studies and is summarized in Table 7.1.

The **magnetic quantum number** (m_ℓ) has integral values between ℓ and $-\ell$, including zero. The value of m_ℓ is related to the orientation of the orbital in space relative to the other orbitals in the atom.

The first four levels of orbitals in the hydrogen atom are listed with their quantum numbers in Table 7.2. Note that each set of orbitals with a given value of ℓ (sometimes called a **subshell**) is designated by giving the value of n and the letter for ℓ . Thus an orbital where $n = 2$ and $\ell = 1$ is symbolized as 2*p*. There are three 2*p* orbitals, which have different orientations in space. We will describe these orbitals in the next section.

$$\begin{aligned}n &= 1, 2, 3, \dots \\ \ell &= 0, 1, \dots, (n - 1) \\ m_\ell &= -\ell, \dots, 0, \dots, +\ell\end{aligned}$$

SAMPLE EXERCISE 7.6**Electron Subshells**

For principal quantum level $n = 5$, determine the number of allowed subshells (different values of ℓ), and give the designation of each.

SOLUTION

For $n = 5$, the allowed values of ℓ run from 0 to 4 ($n - 1 = 5 - 1$). Thus the subshells and their designations are

$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
5s	5p	5d	5f	5g

See Exercises 7.61 through 7.64.

7.7 Orbital Shapes and Energies

We have seen that the meaning of an orbital is represented most clearly by a probability distribution. Each orbital in the hydrogen atom has a unique probability distribution. We also saw that another means of representing an orbital is by the surface that surrounds 90% of the total electron probability. These two types of representations for the hydrogen 1s, 2s, and 3s orbitals are shown in Fig. 7.13. Note the characteristic spherical shape of each of the *s* orbitals. Note also that the 2s and 3s orbitals contain areas of high probability separated by areas of zero probability. These latter areas are called **nodal surfaces**, or simply **nodes**. The number of nodes increases as *n* increases. For *s* orbitals, the number of nodes is given by $n - 1$. For our purposes, however, we will think of *s* orbitals only in terms of their overall spherical shape, which becomes larger as the value of *n* increases.

The two types of representations for the 2*p* orbitals (there are no 1*p* orbitals) are shown in Fig. 7.14. Note that the *p* orbitals are not spherical like *s* orbitals but have two *lobes* separated by a node at the nucleus. The *p* orbitals are labeled according to the axis of the *xyz* coordinate system along which the lobes lie. For example, the 2*p* orbital with lobes centered along the *x* axis is called the 2*p_x* orbital.

As you might expect from our discussion of the *s* orbitals, the 3*p* orbitals have a more complex probability distribution than that of the 2*p* orbitals (see Fig. 7.15), but they can still be represented by the same boundary surface shapes. The surfaces just grow larger as the value of *n* increases.

There are no *d* orbitals that correspond to principal quantum levels $n = 1$ and $n = 2$. The *d* orbitals ($\ell = 2$) first occur in level $n = 3$. The five 3*d* orbitals have the shapes shown in Fig. 7.16. The *d* orbitals have two different fundamental shapes. Four of the orbitals (d_{xz} , d_{yz} , d_{xy} , and $d_{x^2-y^2}$) have four lobes centered in the plane indicated in the orbital label. Note that d_{xy} and $d_{x^2-y^2}$ are both centered in the *xy* plane; however, the lobes of $d_{x^2-y^2}$ lie *along* the *x* and *y* axes, while the lobes of d_{xy} lie *between* the axes. The fifth orbital, d_{z^2} , has a unique shape with two lobes along the *z* axis and a belt centered in the *xy* plane. The *d* orbitals for levels $n > 3$ look like the 3*d* orbitals but have larger lobes.

The *f* orbitals first occur in level $n = 4$, and as might be expected, they have shapes even more complex than those of the *d* orbitals. Figure 7.17 shows representations of the 4*f* orbitals ($\ell = 3$) along with their designations. These orbitals are not involved in the bonding in any of the compounds we will consider in this text. Their shapes and labels are simply included for completeness.

So far we have talked about the shapes of the hydrogen atomic orbitals but not about their energies. For the hydrogen atom, the energy of a particular orbital is determined by its value of *n*. Thus *all* orbitals with the same value of *n* have the *same energy*—they are said to be **degenerate**. This is shown in Fig. 7.18, where the energies for the orbitals in the first three quantum levels for hydrogen are shown.

Hydrogen's single electron can occupy any of its atomic orbitals. However, in the lowest energy state, the *ground state*, the electron resides in the 1s orbital. If energy is put into the atom, the electron can be transferred to a higher-energy orbital, producing an *excited state*.

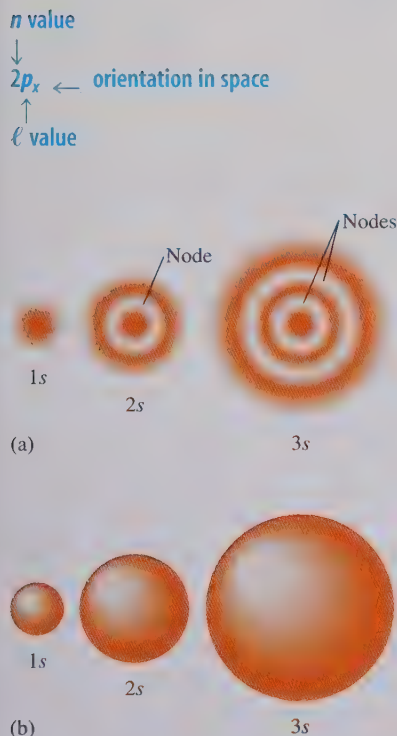
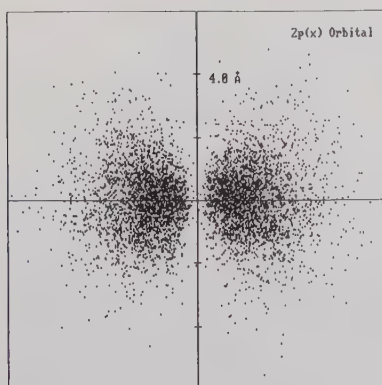


FIGURE 7.13

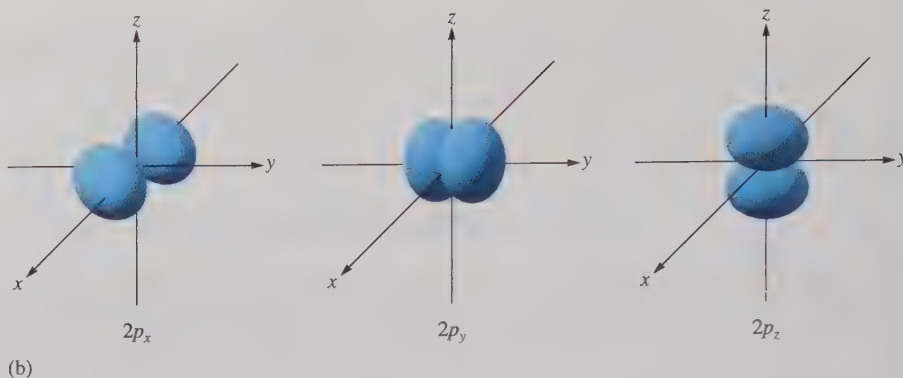
Two representations of the hydrogen 1s, 2s, and 3s orbitals. (a) The electron probability distribution. (b) The surface that contains 90% of the total electron probability (the size of the orbital, by definition).



(a)

FIGURE 7.14Representation of the $2p$ orbitals.(a) The electron probability distribution for a $2p$ orbital.

(Generated from a program by Robert Allen-dorfer on Project SERAPHIM disk PC2402; printed with permission.)

(b) The boundary surface representations of all three $2p$ orbitals.

(b)

A Summary of the Hydrogen Atom

- In the quantum (wave) mechanical model, the electron is viewed as a standing wave. This representation leads to a series of wave functions (orbitals) that describe the possible energies and spatial distributions available to the electron.
- In agreement with the Heisenberg uncertainty principle, the model cannot specify the detailed electron motions. Instead, the square of the wave function represents the probability distribution of the electron in that orbital. This allows us to picture orbitals in terms of probability distributions, or electron density maps.
- The size of an orbital is arbitrarily defined as the surface that contains 90% of the total electron probability.
- The hydrogen atom has many types of orbitals. In the ground state, the single electron resides in the $1s$ orbital. The electron can be excited to higher-energy orbitals if energy is put into the atom.



Visualizations: s orbitals and
Bonding and Antibonding,
 p orbitals

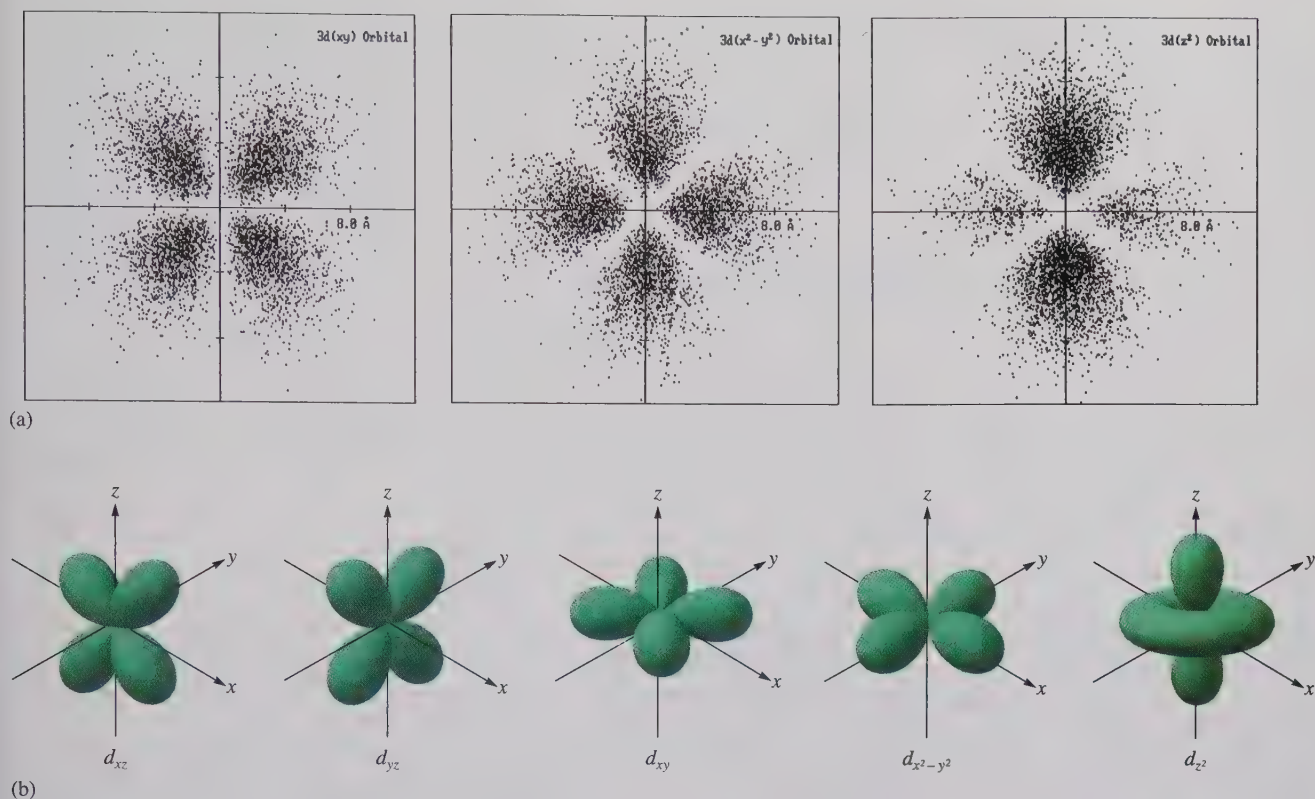
7.8 Electron Spin and the Pauli Principle

The concept of **electron spin** was developed by Samuel Goudsmit and George Uhlenbeck while they were graduate students at the University of Leyden in the Netherlands. They found that a fourth quantum number (in addition to n , ℓ , and m_ℓ) was necessary to account for the details of the emission spectra of atoms. The spectral data indicate that the electron has a magnetic moment with two possible orientations when the atom is placed in an external magnetic field. Since they knew from classical physics that a spinning charge produces a magnetic moment, it seemed reasonable to assume that the electron could have two spin states, thus producing the two oppositely directed magnetic moments (see Fig. 7.19). The new quantum number adopted to describe this phenomenon, called the **electron spin quantum number** (m_s), can have only one of two values, $+\frac{1}{2}$ and $-\frac{1}{2}$. We can interpret this to mean that the electron can spin in one of two opposite directions, although other interpretations also have been suggested.

For our purposes, the main significance of electron spin is connected with the postulate of Austrian physicist Wolfgang Pauli (1900–1958): *In a given atom no two electrons can have the same set of four quantum numbers (n , ℓ , m_ℓ , and m_s).* This is called the **Pauli exclusion principle**. Since electrons in the same orbital have the

FIGURE 7.15

A cross section of the electron probability distribution for a $3p$ orbital.

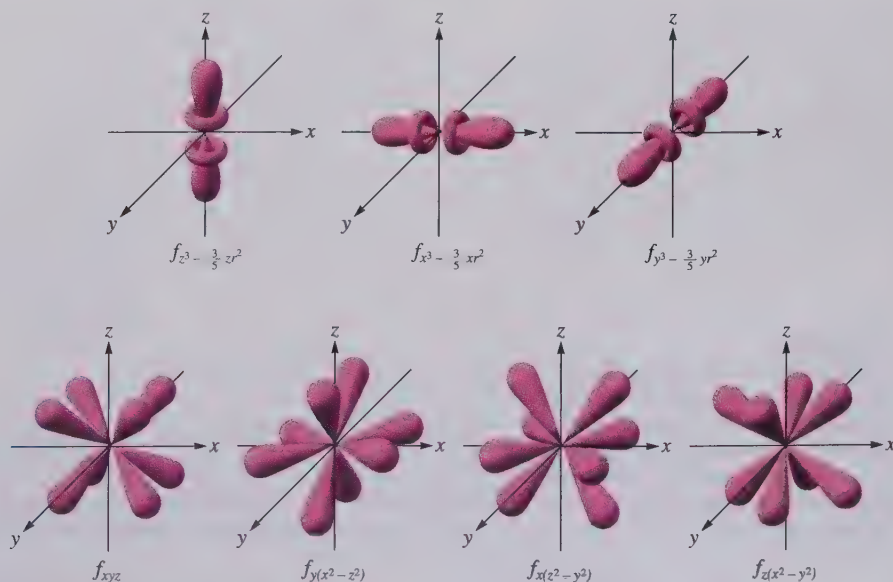
**FIGURE 7.16**

Representation of the 3d orbitals. (a) Electron density plots of selected 3d orbitals.

(Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC2402; printed with permission.)

(b) The boundary surfaces of all of the 3d orbitals.

 Visualization: 3d orbitals

**FIGURE 7.17**

Representation of the 4f orbitals in terms of their boundary surfaces.

$$m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Each orbital can hold a maximum of two electrons.

same values of n , ℓ , and m_ℓ , this postulate says that they must have different values of m_s . Then, since only two values of m_s are allowed, *an orbital can hold only two electrons, and they must have opposite spins*. This principle will have important consequences as we use the atomic model to account for the electron arrangements of the atoms in the periodic table.

7.9 Polyelectronic Atoms

The quantum mechanical model gives a description of the hydrogen atom that agrees very well with experimental data. However, the model would not be very useful if it did not account for the properties of all the other atoms as well.

To see how the model applies to **polyelectronic atoms**, that is, atoms with more than one electron, let's consider helium, which has two protons in its nucleus and two electrons:

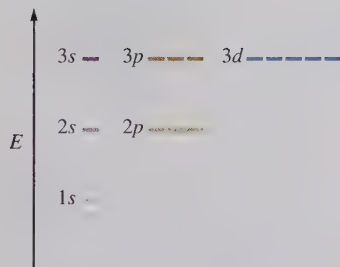


FIGURE 7.18
Orbital energy levels for the hydrogen atom.

Three energy contributions must be considered in the description of the helium atom: (1) the kinetic energy of the electrons as they move around the nucleus, (2) the potential energy of attraction between the nucleus and the electrons, and (3) the potential energy of repulsion between the two electrons.

Although the helium atom can be readily described in terms of the quantum mechanical model, the Schrödinger equation that results cannot be solved exactly. The difficulty arises in dealing with the repulsions between the electrons. Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly. This is called the *electron correlation problem*.

The electron correlation problem occurs with all polyelectronic atoms. To treat these systems using the quantum mechanical model, we must make approximations. Most commonly, the approximation used is to treat each electron as if it were moving in a *field of charge that is the net result of the nuclear attraction and the average repulsions of all the other electrons*.

For example, consider the sodium atom, which has 11 electrons:

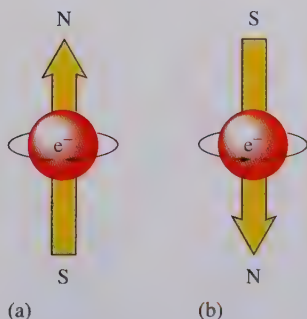
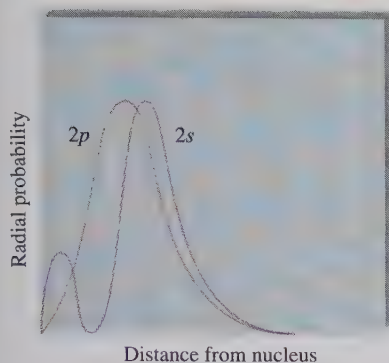


FIGURE 7.19
A picture of the spinning electron. Spinning in one direction, the electron produces the magnetic field oriented as shown in (a). Spinning in the opposite direction, it gives a magnetic field of the opposite orientation, as shown in (b).



Now let's single out the outermost electron and consider the forces this electron feels. The electron clearly is attracted to the highly charged nucleus. However, the electron also feels the repulsions caused by the other 10 electrons. The net effect is that the electron is not bound nearly as tightly to the nucleus as it would be if the

**FIGURE 7.20**

A comparison of the radial probability distributions of the 2s and 2p orbitals.

other electrons were not present. We say that the electron is *screened* or *shielded* from the nuclear charge by the repulsions of the other electrons.

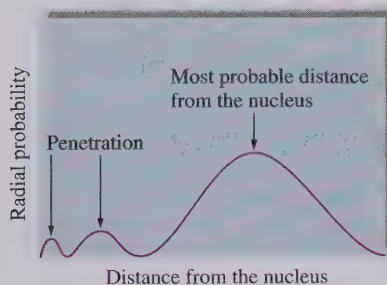
This picture of polyelectronic atoms leads to *hydrogenlike orbitals* for these atoms. They have the same general shapes as the orbitals for hydrogen, but their sizes and energies are different. The differences occur because of the interplay between nuclear attraction and the electron repulsions.

One especially important difference between polyelectronic atoms and the hydrogen atom is that for hydrogen all the orbitals in a given principal quantum level have the same energy (they are said to be *degenerate*). This is not the case for polyelectronic atoms, where we find that for a given principal quantum level the orbitals vary in energy as follows:

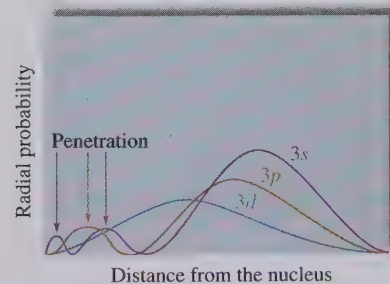
$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

In other words, when electrons are placed in a particular quantum level, they “prefer” the orbitals in the order *s*, *p*, *d*, and then *f*. Why does this happen? Although the concept of orbital energies is a complicated matter, we can qualitatively understand why the 2s orbital has a lower energy than the 2p orbital in a polyelectronic atom by looking at the probability profiles of these orbitals (see Fig. 7.20). Notice that the 2p orbital has its maximum probability closer to the nucleus than for the 2s. This might lead us to predict that the 2p would be preferable (lower energy) to the 2s orbital. However, notice the small hump of electron density that occurs in the 2s profile very near the nucleus. This means that although an electron in the 2s orbital spends most of its time a little farther from the nucleus than does an electron in the 2p orbital, it spends a small but very significant amount of time very near the nucleus. We say that the 2s electron *penetrates* to the nucleus more than one in the 2p orbital. This *penetration effect* causes an electron in a 2s orbital to be attracted to the nucleus more strongly than an electron in a 2p orbital. That is, the 2s orbital is lower in energy than the 2p orbitals in a polyelectronic atom.

The same thing happens in the other principal quantum levels as well. Figure 7.21 shows the radial probability profiles for the 3s, 3p, and 3d orbitals. Note again



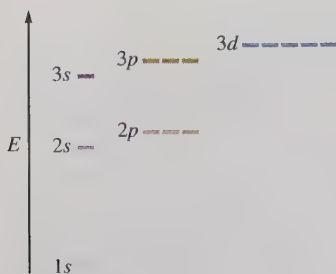
(a)



(b)

FIGURE 7.21

(a) The radial probability distribution for an electron in a 3s orbital. Although a 3s electron is mostly found far from the nucleus, there is a small but significant probability (shown by the arrows) of its being found close to the nucleus. The 3s electron penetrates the shield of inner electrons. (b) The radial probability distribution for the 3s, 3p, and 3d orbitals. The arrows indicate that the s orbital (blue arrow) allows greater electron penetration than the p orbital (red arrow) does; the d orbital allows minimal electron penetration.

**FIGURE 7.22**

The orders of the energies of the orbitals in the first three levels of polyelectronic atoms.

the hump in the 3s profile very near the nucleus. The innermost hump for the 3p is farther out, which causes the energy of the 3s orbital to be lower than that of the 3p. Notice that the 3d orbital has its maximum probability closer to the nucleus than either the 3s or 3p does, but its absence of probability near the nucleus causes it to be highest in energy of the three orbitals. The relative energies of the orbitals for $n = 3$ are

$$E_{3s} < E_{3p} < E_{3d}$$

In general, the more effectively an orbital allows its electron to penetrate the shielding electrons to be close to the nuclear charge, the lower is the energy of that orbital.

A summary diagram of the orders of the orbital energies for polyelectronic atoms is represented in Fig. 7.22. We will use these orbitals in Section 7.11 to show how the electrons are arranged in polyelectronic atoms.

7.10 The History of the Periodic Table

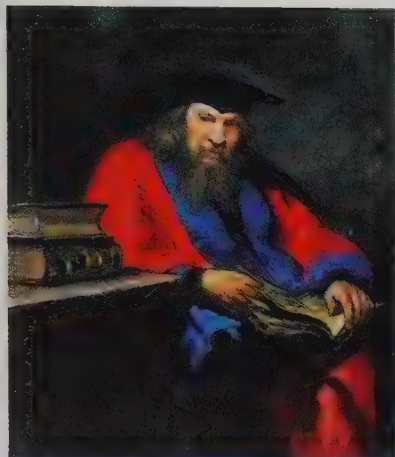
The modern periodic table contains a tremendous amount of useful information. In this section we will discuss the origin of this valuable tool; later we will see how the quantum mechanical model for the atom explains the periodicity of chemical properties. Certainly the greatest triumph of the quantum mechanical model is its ability to account for the arrangement of the elements in the periodic table.

The periodic table was originally constructed to represent the patterns observed in the chemical properties of the elements. As chemistry progressed during the eighteenth and nineteenth centuries, it became evident that the earth is composed of a great many elements with very different properties. Things are much more complicated than the simple model of earth, air, fire, and water suggested by the ancients. At first, the array of elements and properties was bewildering. Gradually, however, patterns were noticed.

The first chemist to recognize patterns was Johann Dobereiner (1780–1849), who found several groups of three elements that have similar properties, for example, chlorine, bromine, and iodine. However, as Dobereiner attempted to expand this model of *triads* (as he called them) to the rest of the known elements, it became clear that it was severely limited.

The next notable attempt was made by the English chemist John Newlands, who in 1864 suggested that elements should be arranged in *octaves*, based on the idea that certain properties seemed to repeat for every eighth element in a way similar to the musical scale, which repeats for every eighth tone. Even though this model managed to group several elements with similar properties, it was not generally successful.

The present form of the periodic table was conceived independently by two chemists: the German Julius Lothar Meyer (1830–1895) and Dmitri Ivanovich Mendeleev (1834–1907), a Russian (Fig. 7.23). Usually Mendeleev is given most of the credit, because it was he who emphasized how useful the table could be in predicting the existence and properties of still unknown elements. For example, in 1872 when Mendeleev first published his table (see Fig. 7.24), the elements gallium, scandium, and germanium were unknown. Mendeleev correctly predicted the existence and properties of these elements from gaps in his periodic table. The data for germanium

**FIGURE 7.23**

Dmitri Ivanovich Mendeleev (1834–1907), born in Siberia as the youngest of 17 children, taught chemistry at the University of St. Petersburg. In 1860 Mendeleev heard the Italian chemist Cannizzaro lecture on a reliable method for determining the correct atomic masses of the elements. This important development paved the way for Mendeleev's own brilliant contribution to chemistry—the periodic table. In 1861 Mendeleev returned to St. Petersburg, where he wrote a book on organic chemistry. Later Mendeleev also wrote a book on inorganic chemistry, and he was struck by the fact that the systematic approach characterizing organic chemistry was lacking in inorganic chemistry. In attempting to systematize inorganic chemistry, he eventually arranged the elements in the form of the periodic table.

Mendeleev was a versatile genius who was interested in many fields of science. He worked on many problems associated with Russia's natural resources, such as coal, salt, and various metals. Being particularly interested in the petroleum industry, he visited the United States in 1876 to study the Pennsylvania oil fields. His interests also included meteorology and hot-air balloons. In 1887 he made an ascent in a balloon to study a total eclipse of the sun.

(which Mendeleev called “*ekasilicon*”) are shown in Table 7.3. Note the excellent agreement between the actual values and Mendeleev's predictions, which were based on the properties of other members in the group of elements similar to germanium.

Using his table, Mendeleev also was able to correct several values for atomic masses. For example, the original atomic mass of 76 for indium was based on the assumption that indium oxide had the formula InO . This atomic mass placed indium, which has metallic properties, among the nonmetals. Mendeleev assumed the atomic mass was probably incorrect and proposed that the formula of indium oxide

TABELLE II

REIHEN	GRUPPE I. — R_2O	GRUPPE II. — RO	GRUPPE III. — R_2O_3	GRUPPE IV. RH_4 RO_2	GRUPPE V. RH_3 R_2O_5	GRUPPE VI. RH_2 RO_3	GRUPPE VII. RH R_2O_7	GRUPPE VIII. — RO_4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	? Di = 138	? Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	—
10	—	—	? Er = 178	? La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	— — — —
12	—	—	—	Th = 231	—	U = 240	—	— — — —

FIGURE 7.24

Mendeleev's early periodic table, published in 1872. Note the spaces left for missing elements with atomic masses 44, 68, 72, and 100.

(From *Annalen der Chemie und Pharmacie*, VIII, Supplementary Volume for 1872, page 511.)

CHEMICAL IMPACT

The Growing Periodic Table

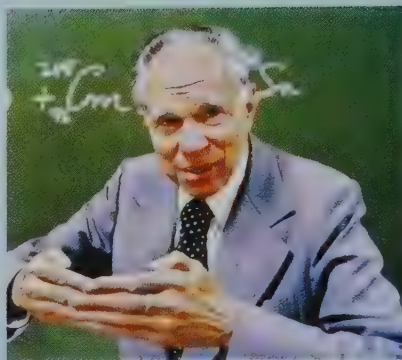
The periodic table of the elements has undergone significant changes since Mendeleev published his first version in 1869. In particular, in the past 60 years we have added 20 new elements beyond uranium. These so-called transuranium elements all have been synthesized using particle accelerators.

Edwin M. McMillan and Phillip H. Abelson succeeded in synthesizing the first transuranium element, neptunium (element 93), at the University of California, Berkeley, in 1940. In 1941, Glenn T. Seaborg synthesized and identified element 94 (plutonium), and over the next several years, researchers under his direction at UC Berkeley discovered nine other transuranium elements. In 1945 Seaborg suggested that the elements heavier than element 89 (actinium) were misplaced as transition metals and should be relocated on the periodic table in a series below the transition metals (the actinide series). Seaborg was awarded a Nobel Prize in chemistry in 1951 for his contributions.

In recent years, three major research facilities have taken the lead in synthesizing new elements. Along with UC Berkeley, Nuclear Research in Dubna, Russia, and GSI in Darmstadt, Germany, were responsible for synthesizing elements 104–112 by the end of 1996.

As it turned out, naming the new elements has caused more controversy than anything else connected with their discovery. Traditionally, the discoverer of an element is allowed to name it. However, because there is some dispute among the researchers at Berkeley, Darmstadt, and Dubna about who really discovered the various elements, competing names were submitted. After years of controversy, the International Union of Pure and Applied Chemistry (IUPAC) finally settled on the names listed in the accompanying table.

The name for element 106 in honor of Glenn Seaborg caused special controversy because an element had never



Dr. Glenn Seaborg.

before been named for a living person (Dr. Seaborg died in 1999). However, because of Seaborg's commanding stature in the scientific community, the name seaborgium was adopted.

Names for the elements beyond 109 have not been decided, and these elements are represented on many periodic tables with three letters that symbolize their atomic numbers. More traditional names will no doubt be assigned in due time (hopefully with a minimum of controversy).

Atomic Number	Name	Symbol
104	Rutherfordium	Rf
105	Dubium	Db
106	Seaborgium	Sg
107	Bohrium	Bh
108	Hassium	Hs
109	Meitnerium	Mt

was really In_2O_3 . Based on this correct formula, indium has an atomic mass of approximately 113, placing the element among the metals. Mendeleev also corrected the atomic masses of beryllium and uranium.

Because of its obvious usefulness, Mendeleev's periodic table was almost universally adopted, and it remains one of the most valuable tools at the chemist's disposal. For example, it is still used to predict the properties of elements yet to be discovered, as shown in Table 7.4.

TABLE 7.3 Comparison of the Properties of Germanium as Predicted by Mendeleev and as Actually Observed

Properties of Germanium	Predicted in 1871	Observed in 1886
Atomic weight	72	72.3
Density	5.5 g/cm ³	5.47 g/cm ³
Specific heat	0.31 J/(°C · g)	0.32 J/(°C · g)
Melting point	Very high	960°C
Oxide formula	RO ₂	GeO ₂
Oxide density	4.7 g/cm ³	4.70 g/cm ³
Chloride formula	RCl ₄	GeCl ₄
bp of chloride	100°C	86°C

TABLE 7.4 Predicted Properties of Elements 113 and 114

Property	Element 113	Element 114
Chemically like	Thallium	Lead
Atomic mass	297	298
Density	16 g/mL	14 g/mL
Melting point	430°C	70°C
Boiling point	1100°C	150°C

A current version of the periodic table is shown inside the front cover of this book. The only fundamental difference between this table and that of Mendeleev is that it lists the elements in order by atomic number rather than by atomic mass. The reason for this will become clear later in this chapter as we explore the electron arrangements of the atom. Another recent format of the table is discussed in the following section.

7.11 The Aufbau Principle and the Periodic Table

We can use the quantum mechanical model of the atom to show how the electron arrangements in the hydrogenlike atomic orbitals of the various atoms account for the organization of the periodic table. Our main assumption here is that all atoms have the same type of orbitals as have been described for the hydrogen atom. As *protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogenlike orbitals*. This is called the **aufbau principle**.

Hydrogen has one electron, which occupies the 1s orbital in its ground state. The configuration for hydrogen is written as 1s¹, which can be represented by the following *orbital diagram*:

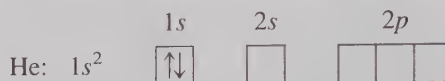


The arrow represents an electron spinning in a particular direction.

Aufbau is German for "building up."

H ($Z = 1$)
 He ($Z = 2$)
 Li ($Z = 3$)
 Be ($Z = 4$)
 B ($Z = 5$)
 etc.
 ($Z = \text{atomic number}$)

The next element, *helium*, has two electrons. Since two electrons with opposite spins can occupy an orbital, according to the Pauli exclusion principle, the electrons for helium are in the $1s$ orbital with opposite spins, producing a $1s^2$ configuration:



Lithium has three electrons, two of which can go into the $1s$ orbital before the orbital is filled. Since the $1s$ orbital is the only orbital for $n = 1$, the third electron will occupy the lowest-energy orbital with $n = 2$, or the $2s$ orbital, giving a $1s^2 2s^1$ configuration:



The next element, *beryllium*, has four electrons, which occupy the $1s$ and $2s$ orbitals:



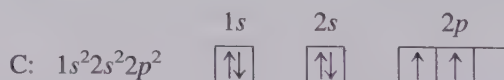
Boron has five electrons, four of which occupy the $1s$ and $2s$ orbitals. The fifth electron goes into the second type of orbital with $n = 2$, the $2p$ orbitals:



Since all the $2p$ orbitals have the same energy (are degenerate), it does not matter which $2p$ orbital the electron occupies.

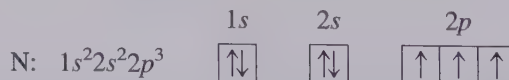
Carbon is the next element and has six electrons. Two electrons occupy the $1s$ orbital, two occupy the $2s$ orbital, and two occupy $2p$ orbitals. Since there are three $2p$ orbitals with the same energy, the mutually repulsive electrons will occupy *separate* $2p$ orbitals. This behavior is summarized by **Hund's rule** (named for the German physicist F. H. Hund), which states that *the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals*. By convention, the unpaired electrons are represented as having parallel spins (with spin "up").

The configuration for carbon could be written $1s^2 2s^2 2p^1 2p^1$ to indicate that the electrons occupy separate $2p$ orbitals. However, the configuration is usually given as $1s^2 2s^2 2p^2$, and it is understood that the electrons are in different $2p$ orbitals. The orbital diagram for carbon is



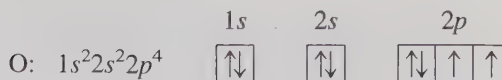
Note that the unpaired electrons in the $2p$ orbitals are shown with parallel spins.

The configuration for *nitrogen*, which has seven electrons, is $1s^2 2s^2 2p^3$. The three electrons in the $2p$ orbitals occupy separate orbitals with parallel spins:



The configuration for *oxygen*, which has eight electrons, is $1s^2 2s^2 2p^4$. One of the $2p$ orbitals is now occupied by a pair of electrons with opposite spins, as required by the Pauli exclusion principle:

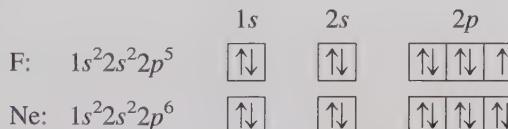
For an atom with unfilled subshells, the lowest energy is achieved by electrons occupying separate orbitals with parallel spins, as far as allowed by the Pauli exclusion principle.



[Ne] is shorthand for $1s^2 2s^2 2p^6$.



Sodium metal is so reactive that it is stored under kerosene to protect it from the oxygen in the air.



With neon, the orbitals with $n = 1$ and $n = 2$ are now completely filled.

For *sodium*, the first ten electrons occupy the $1s$, $2s$, and $2p$ orbitals, and the eleventh electron must occupy the first orbital with $n = 3$, the $3s$ orbital. The electron configuration for sodium is $1s^2 2s^2 2p^6 3s^1$. To avoid writing the inner-level electrons, this configuration is often abbreviated as $[\text{Ne}]3s^1$, where $[\text{Ne}]$ represents the electron configuration of neon, $1s^2 2s^2 2p^6$.

The next element, *magnesium*, has the configuration $1s^2 2s^2 2p^6 3s^2$, or $[\text{Ne}] 3s^2$. Then the next six elements, *aluminum* through *argon*, have configurations obtained by filling the $3p$ orbitals one electron at a time. Figure 7.25 summarizes the electron configurations of the first 18 elements by giving the number of electrons in the type of orbital occupied last.

At this point it is useful to introduce the concept of **valence electrons**, *the electrons in the outermost principal quantum level of an atom*. The valence electrons of the nitrogen atom, for example, are the $2s$ and $2p$ electrons. For the sodium atom, the valence electron is the electron in the $3s$ orbital, and so on. Valence electrons are the most important electrons to chemists because they are involved in bonding, as we will see in the next two chapters. The inner electrons are known as **core electrons**.

Note in Fig. 7.25 that a very important pattern is developing: *The elements in the same group (vertical column of the periodic table) have the same valence electron configuration.* Remember that Mendeleev originally placed the elements in groups based on similarities in chemical properties. Now we understand the reason behind these groupings. Elements with the same valence electron configuration show similar chemical behavior.

The element after argon is *potassium*. Since the $3p$ orbitals are fully occupied in argon, we might expect the next electron to go into a $3d$ orbital (recall that for $n = 3$ the orbitals are $3s$, $3p$, and $3d$). However, the chemistry of potassium is clearly very similar to that of lithium and sodium, indicating that the last electron in potassium occupies the $4s$ orbital instead of one of the $3d$ orbitals, a conclusion

H 1s ¹							He 1s ²
Li 2s ¹	Be 2s ²						
Na 3s ¹	Mg 3s ²						
		B 2p ¹	C 2p ²	N 2p ³	O 2p ⁴	F 2p ⁵	Ne 2p ⁶
		Al 3p ¹	Si 3p ²	P 3p ³	S 3p ⁴	Cl 3p ⁵	Ar 3p ⁶

FIGURE 7.25
The electron configurations in the type of orbital occupied last for the first 18 elements.

confirmed by many types of experiments. The electron configuration of potassium is



The next element is *calcium*:



The next element, *scandium*, begins a series of 10 elements (scandium through zinc) called the **transition metals**, whose configurations are obtained by adding electrons to the five *3d* orbitals. The configuration of scandium is



That of *titanium* is



And that of *vanadium* is

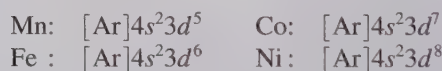


Chromium is the next element. The expected configuration is $[\text{Ar}]4s^2 3d^4$. However, the observed configuration is



The explanation for this configuration of chromium is beyond the scope of this book. In fact, chemists are still disagreeing over the exact cause of this anomaly. Note, however, that the observed configuration has both the *4s* and *3d* orbitals half-filled. This is a good way to remember the correct configuration.

The next four elements, *manganese* through *nickel*, have the expected configurations:



The configuration for *copper* is expected to be $[\text{Ar}]4s^2 3d^9$. However, the observed configuration is



In this case, a half-filled *4s* orbital and a filled set of *3d* orbitals characterize the actual configuration.

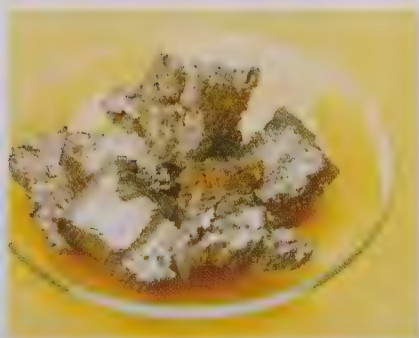
Zinc has the expected configuration:



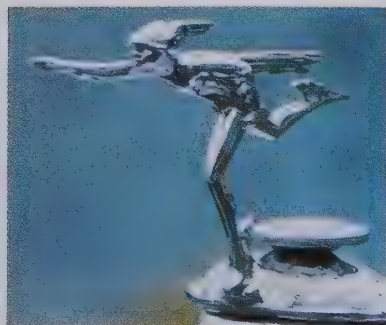
The configurations of the transition metals are shown in Fig. 7.26. After that, the next six elements, *gallium* through *krypton*, have configurations that correspond to filling the *4p* orbitals (see Fig. 7.26).

The entire periodic table is represented in Fig. 7.27 in terms of which orbitals are being filled. The valence electron configurations are given in Fig. 7.28. From these two figures, note the following additional points:

1. The $(n + 1)s$ orbitals always fill before the *nd* orbitals. For example, the *5s* orbitals fill in rubidium and strontium before the *4d* orbitals fill in the second row of transition metals (yttrium through cadmium). This early filling of the *s* orbitals can be explained by the penetration effect. For example, the *4s* orbital allows for so much more penetration to the vicinity of the nucleus that it becomes lower in energy than the *3d* orbital. Thus the *4s* fills before the *3d*. The



Calcium metal.



Chromium is often used to plate bumpers and hood ornaments, such as this statue of Mercury found on a 1929 Buick.

The $(n + 1)s$ orbital fills before the *nd* orbitals.

K 4s ¹	Ca 4s ²	Sc 3d ¹	Ti 3d ²	V 3d ³	Cr 4s ¹ 3d ⁵	Mn 3d ⁵	Fe 3d ⁶	Co 3d ⁷	Ni 3d ⁸	Cu 4s ¹ 3d ¹⁰	Zn 3d ¹⁰	Ga 4p ¹	Ge 4p ²	As 4p ³	Se 4p ⁴	Br 4p ⁵	Kr 4p ⁶

FIGURE 7.26

Electron configurations for potassium through krypton. The transition metals (scandium through zinc) have the general configuration $[\text{Ar}]4s^23d^n$, except for chromium and copper.

Lanthanides are elements in which the 4f orbitals are being filled.

Actinides are elements in which the 5f orbitals are being filled.

same things can be said about the 5s and 4d, the 6s and 5d, and the 7s and 6d orbitals.

- After lanthanum, which has the configuration $[\text{Xe}]6s^25d^1$, a group of 14 elements called the **lanthanide series**, or the **lanthanides**, occurs. This series of elements corresponds to the filling of the seven 4f orbitals. Note that sometimes an electron occupies a 5d orbital instead of a 4f orbital. This occurs because the energies of the 4f and 5d orbitals are very similar.
- After actinium, which has the configuration $[\text{Rn}]7s^26d^1$, a group of 14 elements called the **actinide series**, or the **actinides**, occurs. This series corresponds to the filling of the seven 5f orbitals. Note that sometimes one or two electrons occupy the 6d orbitals instead of the 5f orbitals, because these orbitals have very similar energies.
- The group labels for Groups 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A indicate the *total number* of valence electrons for the atoms in these groups. For example,

		Group																
Period	1	1A	1s	2A									3A	4A	5A	6A	7A	8A
	2		2s													2p		
	3		3s													3p		
	4		4s					3d								4p		
	5		5s					4d								5p		
	6		6s	La				5d								6p		
	7		7s	Ac				6d										

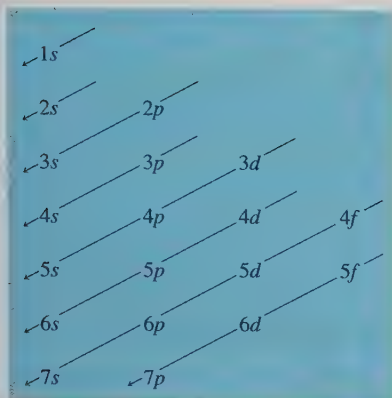
The group label tells the total number of valence electrons for that group.

The periodic table with atomic symbols, atomic numbers, and partial electron configurations.

all the elements in Group 5A have the configuration ns^2np^3 . (The d electrons fill one period late and are usually not counted as valence electrons.) The meaning of the group labels for the transition metals is not as clear as for the Group A elements, and these will not be used in this text.

5. The groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A are often called the **main-group**, or **representative, elements**. Every member of these groups has the same valence electron configuration.

The International Union of Pure and Applied Chemistry (IUPAC), a body of scientists organized to standardize scientific conventions, has recommended a new form for the periodic table, which the American Chemical Society has adopted (see the blue numbers in Fig. 7.28). In this new version the group number indicates

**FIGURE 7.29**

A diagram that summarizes the order in which the orbitals fill in polyelectronic atoms.

When an electron configuration is given in this text, the orbitals are listed in the order in which they fill.

Cr: $[\text{Ar}]4s^13d^5$

Cu: $[\text{Ar}]4s^13d^{10}$

SAMPLE EXERCISE 7.7

the number of s , p , and d electrons added since the last noble gas. We will not use the new format in this book, but you should be aware that the familiar periodic table may be soon replaced by this or a similar format.

The results considered in this section are very important. We have seen that the quantum mechanical model can be used to explain the arrangement of the elements in the periodic table. This model allows us to understand that the similar chemistry exhibited by the members of a given group arises from the fact that they all have the same valence electron configuration. Only the principal quantum number of the valence orbitals changes in going down a particular group.

It is important to be able to give the electron configuration for each of the main-group elements. This is most easily done by using the periodic table. If you understand how the table is organized, it is not necessary to memorize the order in which the orbitals fill. Review Figs. 7.27 and 7.28 to make sure that you understand the correspondence between the orbitals and the periods and groups.

Predicting the configurations of the transition metals ($3d$, $4d$, and $5d$ elements), the lanthanides ($4f$ elements), and the actinides ($5f$ elements) is somewhat more difficult because there are many exceptions of the type encountered in the first-row transition metals (the $3d$ elements). You should memorize the configurations of chromium and copper, the two exceptions in the first-row transition metals, since these elements are often encountered.

A diagram that is often used to summarize the order in which the orbitals are filled in polyelectronic atoms is shown in Fig. 7.29. Note that this diagram is generated by listing horizontally the orbitals in a given principal quantum level and then drawing diagonal arrows to show the order of filling.

Electron Configurations

Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra) using the periodic table inside the front cover of this book.

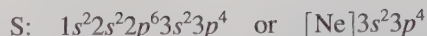
SOLUTION

Sulfur is element 16 and resides in Period 3, where the $3p$ orbitals are being filled (see Fig. 7.30). Since sulfur is the fourth among the “ $3p$ elements,” it must have four $3p$ electrons. Its configuration is

		Group																	
Period	1A																8A		
	1	1s	2A											3A	4A	5A	6A	7A	1s
	2	2s											2p						
	3	3s											3p					S	
	4	4s					3d					4p							
	5	5s					4d					Cd	5p						
	6	6s	La	Hf					5d					6p					
	7	7s	Ra	Ac					6d										
														4f					
														5f					

FIGURE 7.30

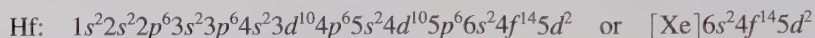
The positions of the elements considered in Sample Exercise 7.7.



Cadmium is element 48 and is located in Period 5 at the end of the 4*d* transition metals, as shown in Fig. 7.30. It is the tenth element in the series and thus has 10 electrons in the 4*d* orbitals, in addition to the 2 electrons in the 5*s* orbital. The configuration is



Hafnium is element 72 and is found in Period 6, as shown in Fig. 7.30. Note that it occurs just after the lanthanide series. Thus the 4*f* orbitals are already filled. Hafnium is the second member of the 5*d* transition series and has two 5*d* electrons. The configuration is



Radium is element 88 and is in Period 7 (and Group 2A), as shown in Fig. 7.30. Thus radium has two electrons in the 7*s* orbital, and the configuration is



See Exercises 7.71 through 7.74.

7.12 Periodic Trends in Atomic Properties

We have developed a fairly complete picture of polyelectronic atoms. Although the model is rather crude because the nuclear attractions and electron repulsions are simply lumped together, it is very successful in accounting for the periodic table of elements. We will next use the model to account for the observed trends in several important atomic properties: ionization energy, electron affinity, and atomic size.

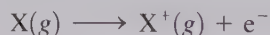
Ionization energy results in the formation of a positive ion.



Setting the aluminum cap on the Washington Monument in 1884. At that time, aluminum was regarded as a precious metal.

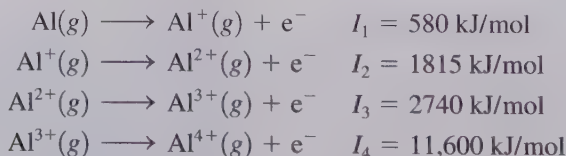
Ionization Energy

Ionization energy is the energy required to remove an electron from a gaseous atom or ion:



where the atom or ion is assumed to be in its ground state.

To introduce some of the characteristics of ionization energy, we will consider the energy required to remove several electrons in succession from aluminum in the gaseous state. The ionization energies are



Several important points can be illustrated from these results. In a stepwise ionization process, it is always the highest-energy electron (the one bound least tightly) that is removed first. The **first ionization energy** I_1 is the energy required to remove the highest-energy electron of an atom. The first electron removed from the aluminum atom comes from the 3*p* orbital (Al has the electron configuration $[\text{Ne}] 3s^2 3p^1$). The second electron comes from the 3*s* orbital (since Al^+ has the configuration $[\text{Ne}] 3s^2$).

Note that the value of I_1 is considerably smaller than the value of I_2 , the **second ionization energy**.

This makes sense for several reasons. The primary factor is simply charge. Note that the first electron is removed from a neutral atom (Al), whereas the second electron is removed from a $1+$ ion (Al^+). The increase in positive charge binds the electrons more firmly, and the ionization energy increases. The same trend shows up in the third (I_3) and fourth (I_4) ionization energies, where the electron is removed from the Al^{2+} and Al^{3+} ions, respectively.

The increase in successive ionization energies for an atom also can be interpreted using our simple model for polyelectronic atoms. The increase in ionization energy from I_1 to I_2 makes sense because the first electron is removed from a $3p$ orbital that is higher in energy than the $3s$ orbital from which the second electron is removed. The largest jump in ionization energy by far occurs in going from the third ionization energy (I_3) to the fourth (I_4). This is so because I_4 corresponds to removing a core electron (Al^{3+} has the configuration $1s^2 2s^2 2p^6$), and core electrons are bound much more tightly than valence electrons.

Table 7.5 gives the values of ionization energies for all the Period 3 elements. Note the large jump in energy in each case in going from removal of valence electrons to removal of core electrons.

The values of the first ionization energies for the elements in the first six periods of the periodic table are graphed in Fig. 7.31. Note that in general as we go *across a period from left to right, the first ionization energy increases*. This is consistent with the idea that electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons. Thus electrons in the same principal quantum level are generally more strongly bound as we move to the right on the periodic table, and there is a general increase in ionization energy values as electrons are added to a given principal quantum level.

On the other hand, *first ionization energy decreases in going down a group*. This can be seen most clearly by focusing on the Group 1A elements (the alkali metals) and the Group 8A elements (the noble gases), as shown in Table 7.6. The main reason for the decrease in ionization energy in going down a group is that the electrons being removed are, on average, farther from the nucleus. As n increases, the size of the orbital increases, and the electron is easier to remove.

First ionization energy increases across a period and decreases down a group.

TABLE 7.5 Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

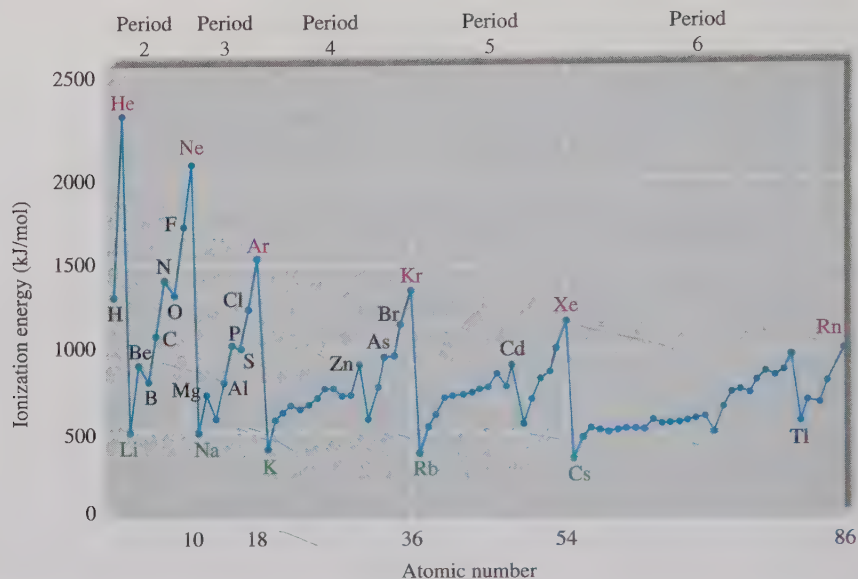


TABLE 7.6 First Ionization Energies for the Alkali Metals and Noble Gases

Atom	I_1 (kJ/mol)
Group 1A	
Li	520
Na	495
K	419
Rb	409
Cs	382
Group 8A	
He	2377
Ne	2088
Ar	1527
Kr	1356
Xe	1176
Rn	1042

FIGURE 7.31

The values of first ionization energy for the elements in the first six periods. In general, ionization energy decreases in going down a group. For example, note the decrease in values for Group 1A and Group 8A. In general, ionization energy increases in going left to right across a period. For example, note the sharp increase going across Period 2 from lithium through neon.

In Fig. 7.31 we see that there are some discontinuities in ionization energy in going across a period. For example, for Period 2, discontinuities occur in going from beryllium to boron and from nitrogen to oxygen. These exceptions to the normal trend can be explained in terms of electron repulsions. The decrease in ionization energy in going from beryllium to boron reflects the fact that the electrons in the filled $2s$ orbital provide some shielding for electrons in the $2p$ orbital from the nuclear charge. The decrease in ionization energy in going from nitrogen to oxygen reflects the extra electron repulsions in the doubly occupied oxygen $2p$ orbital.

The ionization energies for the representative elements are summarized in Fig. 7.32.

FIGURE 7.32
Trends in ionization energies (kJ/mol) for the representative elements.

	1A	2A		3A	4A	5A	6A	7A	8A
1	H 1311								He 2377
2	Li 520	Be 899		B 800	C 1086	N 1402	O 1314	F 1681	Ne 2088
3	Na 495	Mg 735		Al 580	Si 780	P 1060	S 1005	Cl 1255	Ar 1527
4	K 419	Ca 590		Ga 579	Ge 761	As 947	Se 941	Br 1143	Kr 1356
5	Rb 409	Sr 549		In 558	Sn 708	Sb 834	Te 869	I 1009	Xe 1176
6	Cs 382	Ba 503		Tl 589	Pb 715	Bi 703	Po 813	At (926)	Rn 1042

SAMPLE EXERCISE 7.8

Trends in Ionization Energies

The first ionization energy for phosphorus is 1060 kJ/mol, and that for sulfur is 1005 kJ/mol. Why?

SOLUTION

Phosphorus and sulfur are neighboring elements in Period 3 of the periodic table and have the following valence electron configurations: Phosphorus is $3s^23p^3$, and sulfur is $3s^23p^4$.

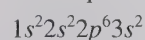
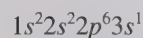
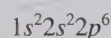
Ordinarily, the first ionization energy increases as we go across a period, so we might expect sulfur to have a greater ionization energy than phosphorus. However, in this case the fourth p electron in sulfur must be placed in an already occupied orbital. The electron–electron repulsions that result cause this electron to be more easily removed than might be expected.

See Question 7.27 and Exercise 7.93.

SAMPLE EXERCISE 7.9

Ionization Energies

Consider atoms with the following electron configurations:



Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

SOLUTION

The atom with the largest value of I_1 is the one with the configuration $1s^22s^22p^6$ (this is the neon atom), because this element is found at the right end of Period 2. Since the $2p$ electrons do not shield each other very effectively, I_1 will be relatively large. The other configurations given include $3s$ electrons. These electrons are effectively shielded by the core electrons and are farther from the nucleus than the $2p$ electrons in neon. Thus I_1 for these atoms will be smaller than for neon.

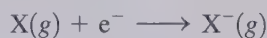
The atom with the smallest value of I_2 is the one with the configuration $1s^22s^22p^63s^2$ (the magnesium atom). For magnesium, both I_1 and I_2 involve valence electrons. For the atom with the configuration $1s^22s^22p^63s^1$ (sodium), the second electron lost (corresponding to I_2) is a core electron (from a $2p$ orbital).

See Question 7.28 and Exercise 7.123.

Electron Affinity

Electron affinity is associated with the production of a negative ion.

Electron affinity is the energy change associated with the addition of an electron to a gaseous atom:

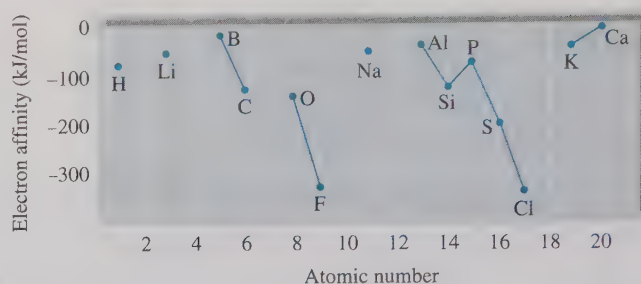


The sign convention for electron affinity values follows the convention for energy changes used in Chapter 6.

Because two different conventions have been used, there is a good deal of confusion in the chemical literature about the signs for electron affinity values. Electron affinity has been defined in many textbooks as the energy *released* when an

FIGURE 7.33

The electron affinity values for atoms among the first 20 elements that form stable, isolated X^- ions. The lines shown connect adjacent elements. The absence of a line indicates missing elements (He, Be, N, Ne, Mg, and Ar) whose atoms do not add an electron exothermically and thus do not form stable, isolated X^- ions.



electron is added to a gaseous atom. This convention requires that a positive sign be attached to an exothermic addition of an electron to an atom, which opposes normal thermodynamic conventions. Therefore, in this book we define electron affinity as a *change* in energy, which means that if the addition of the electron is exothermic, the corresponding value for electron affinity will carry a negative sign.

Figure 7.33 shows the electron affinity values for the atoms among the first 20 elements that form stable, isolated negative ions—that is, the atoms that undergo the addition of an electron as shown above. As expected, all these elements have negative (exothermic) electron affinities. Note that the *more negative* the energy, the greater the quantity of energy released. Although electron affinities generally become more negative from left to right across a period, there are several exceptions to this rule in each period. The dependence of electron affinity on atomic number can be explained by considering the changes in electron repulsions as a function of electron configurations. For example, the fact that the nitrogen atom does not form a stable, isolated $N^-(g)$ ion, whereas carbon forms $C^-(g)$, reflects the difference in the electron configurations of these atoms. An electron added to nitrogen ($1s^2 2s^2 2p^3$) to form the $N^-(g)$ ion ($1s^2 2s^2 2p^4$) would have to occupy a $2p$ orbital that already contains one electron. The extra repulsion between the electrons in this doubly occupied orbital causes $N^-(g)$ to be unstable. When an electron is added to carbon ($1s^2 2s^2 2p^2$) to form the $C^-(g)$ ion ($1s^2 2s^2 2p^3$), no such extra repulsions occur.

In contrast to the nitrogen atom, the oxygen atom can add one electron to form the stable $O^-(g)$ ion. Presumably oxygen's greater nuclear charge compared with that of nitrogen is sufficient to overcome the repulsion associated with putting a second electron into an already occupied $2p$ orbital. However, it should be noted that a second electron *cannot* be added to an oxygen atom [$O^-(g) + e^- \nrightarrow O^{2-}(g)$] to form an isolated oxide ion. This outcome seems strange in view of the many stable oxide compounds (MgO , Fe_2O_3 , and so on) that are known. As we will discuss in detail in Chapter 8, the O^{2-} ion is stabilized in ionic compounds by the large attractions that occur among the positive ions and the oxide ions.

When we go down a group, electron affinity should become more positive (less energy released), since the electron is added at increasing distances from the nucleus. Although this is generally the case, the changes in electron affinity in going down most groups are relatively small, and numerous exceptions occur. This behavior is demonstrated by the electron affinities of the Group 7A elements (the halogens) shown in Table 7.7. Note that the range of values is quite small compared with the changes that typically occur across a period. Also note that although chlorine,

TABLE 7.7 Electron Affinities of the Halogens

Atom	Electron Affinity (kJ/mol)
F	-327.8
Cl	-348.7
Br	-324.5
I	-295.2



Liquid bromine in equilibrium with its vapor.

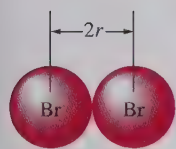


FIGURE 7.34
The radius of an atom (r) is defined as half the distance between the nuclei in a molecule consisting of identical atoms.

bromine, and iodine show the expected trend, the energy released when an electron is added to fluorine is smaller than might be expected. This smaller energy release has been attributed to the small size of the $2p$ orbitals. Because the electrons must be very close together in these orbitals, there are unusually large electron–electron repulsions. In the other halogens with their larger orbitals, the repulsions are not as severe.

Atomic Radius

Just as the size of an orbital cannot be specified exactly, neither can the size of an atom. We must make some arbitrary choices to obtain values for **atomic radii**. These values can be obtained by measuring the distances between atoms in chemical compounds. For example, in the bromine molecule, the distance between the two nuclei is known to be 228 pm. The bromine atomic radius is assumed to be half this distance, or 114 pm, as shown in Fig. 7.34. These radii are often called *covalent atomic radii* because of the way they are determined (from the distances between atoms in covalent bonds).

For nonmetallic atoms that do not form diatomic molecules, the atomic radii are estimated from their various covalent compounds. The radii for metal atoms (called *metallic radii*) are obtained from half the distance between metal atoms in solid metal crystals.

The values of the atomic radii for the representative elements are shown in Fig. 7.35. Note that these values are significantly smaller than might be expected from the 90% electron density volumes of isolated atoms, because when atoms form bonds, their electron “clouds” interpenetrate. However, these values form a self-consistent data set that can be used to discuss the trends in atomic radii.

Note from Fig. 7.35 that the atomic radii decrease in going from left to right across a period. This decrease can be explained in terms of the increasing effective nuclear charge (decreasing shielding) in going from left to right. This means that the valence electrons are drawn closer to the nucleus, decreasing the size of the atom.

Atomic radius increases down a group, because of the increases in the orbital sizes in successive principal quantum levels.

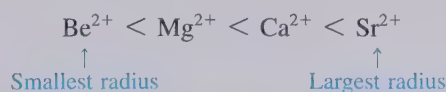
SAMPLE EXERCISE 7.10

Trends in Radii

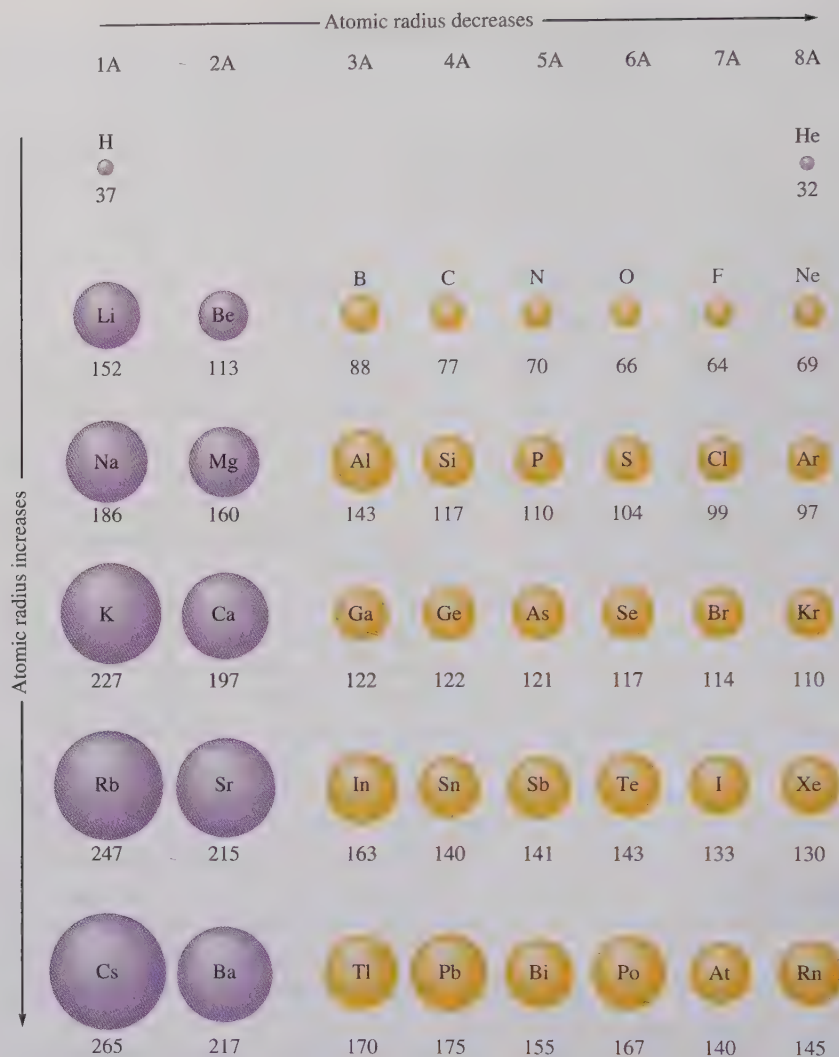
Predict the trend in radius for the following ions: Be^{2+} , Mg^{2+} , Ca^{2+} , and Sr^{2+} .

SOLUTION

All these ions are formed by removing two electrons from an atom of a Group 2A element. In going from beryllium to strontium, we are going down the group, so the sizes increase:



See Exercises 7.85, 7.86, and 7.89.

**FIGURE 7.35**

Atomic radii (in picometers) for selected atoms. Note that atomic radius decreases going across a period and increases going down a group. The values for the noble gases are estimated, because data from bonded atoms are lacking.

7.13 The Properties of a Group: The Alkali Metals

We have seen that the periodic table originated as a way to portray the systematic properties of the elements. Mendeleev was primarily responsible for first showing its usefulness in correlating and predicting the elemental properties. In this section we will summarize much of the information available from the table. We also will illustrate the usefulness of the table by discussing the properties of a representative group, the alkali metals.

Information Contained in the Periodic Table

1. The essence of the periodic table is that the groups of representative elements exhibit similar chemical properties that change in a regular way. The quantum mechanical model of the atom has allowed us to understand the basis for the

similarity of properties in a group—that each group member has the same valence electron configuration. *It is the number and type of valence electrons that primarily determine an atom's chemistry.*

2. One of the most valuable types of information available from the periodic table is the electron configuration of any representative element. If you understand the organization of the table, you will not need to memorize electron configurations for these elements. Although the predicted electron configurations for transition metals are sometimes incorrect, this is not a serious problem. You should, however, memorize the configurations of two exceptions, chromium and copper, since these 3*d* transition elements are found in many important compounds.
3. As we mentioned in Chapter 2, certain groups in the periodic table have special names. These are summarized in Fig. 7.36. Groups are often referred to by these names, so you should learn them.

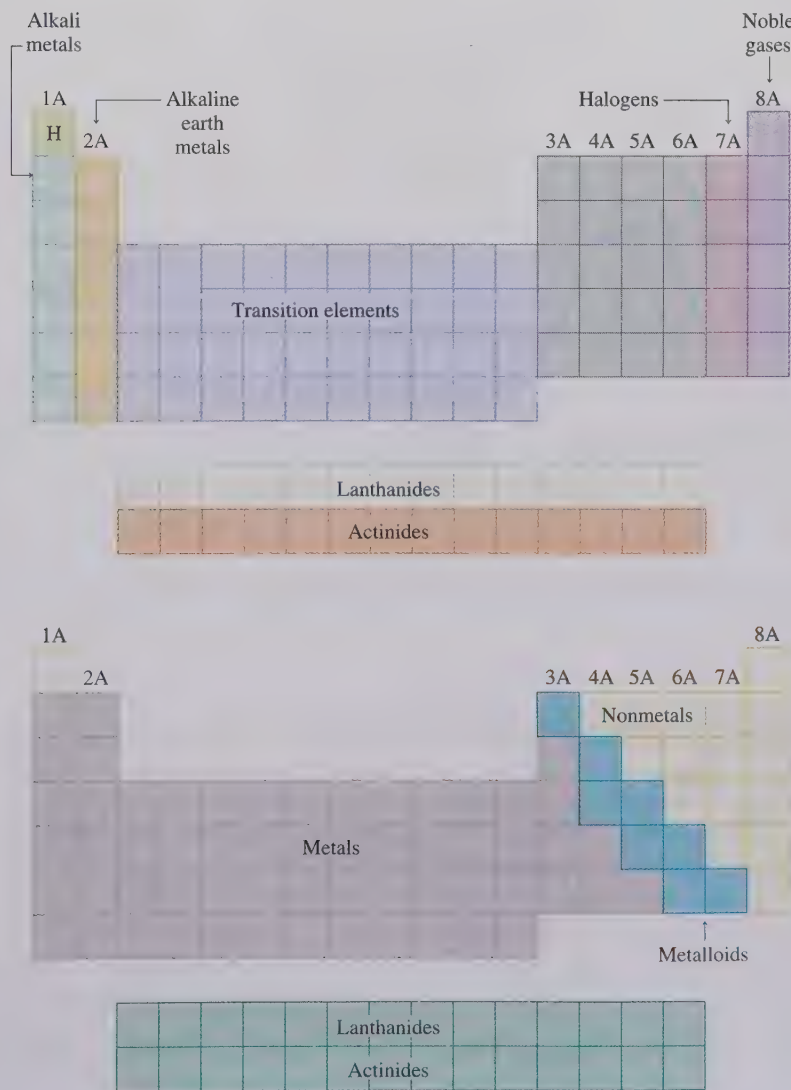


FIGURE 7.36
Special names for groups in the periodic table.

Metals and nonmetals were first discussed in Chapter 2.

- The most basic division of the elements in the periodic table is into metals and nonmetals. The most important chemical property of a metal atom is the tendency to give up one or more electrons to form a positive ion; metals tend to have low ionization energies. The metallic elements are found on the left side of the table, as shown in Fig. 7.36. The most chemically reactive metals are found on the lower left-hand portion of the table, where the ionization energies are smallest. The most distinctive chemical property of a nonmetal atom is the ability to gain one or more electrons to form an anion when reacting with a metal. Thus nonmetals are elements with large ionization energies and the most negative electron affinities. The nonmetals are found on the right side of the table, with the most reactive ones in the upper right-hand corner, except for the noble gas elements, which are quite unreactive. The division into metals and nonmetals shown in Fig. 7.36 is only approximate. Many elements along the division line exhibit both metallic and nonmetallic properties under certain circumstances. These elements are often called **metalloids**, or sometimes **semimetals**.

The Alkali Metals

The metals of Group 1A, the alkali metals, illustrate very well the relationships among the properties of the elements in a group. Lithium, sodium, potassium, rubidium, cesium, and francium are the most chemically reactive of the metals. We will not discuss francium here because it occurs in nature in only very small quantities. Although hydrogen is found in Group 1A of the periodic table, it behaves as a nonmetal, in contrast to the other members of that group. The fundamental reason for hydrogen's nonmetallic character is its very small size (see Fig. 7.35). The electron in the small $1s$ orbital is bound tightly to the nucleus.

Some important properties of the first five alkali metals are shown in Table 7.8. The data in Table 7.8 show that in going down the group, the first ionization energy decreases and the atomic radius increases. This agrees with the general trends discussed in Section 7.12.

The overall increase in density in going down Group 1A is typical of all groups. This occurs because atomic mass generally increases more rapidly than atomic size. Thus there is more mass per unit volume for each succeeding element.

The smooth decrease in melting point and boiling point in going down Group 1A is not typical; in most other groups more complicated behavior occurs. Note that

Hydrogen will be discussed further in Chapter 19.

Other groups will be discussed in Chapters 19 and 20.

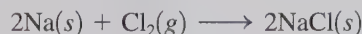
TABLE 7.8 Properties of Five Alkali Metals

Element	Valence Electron Configuration	Density at 25°C (g/cm ³)	mp (°C)	bp (°C)	First Ionization Energy (kJ/mol)	Atomic (covalent) Radius (pm)	Ionic (M ⁺) Radius (pm)
Li	2s ¹	0.53	180	1330	520	152	60
Na	3s ¹	0.97	98	892	495	186	95
K	4s ¹	0.86	64	760	419	227	133
Rb	5s ¹	1.53	39	668	409	247	148
Cs	6s ¹	1.87	29	690	382	265	169

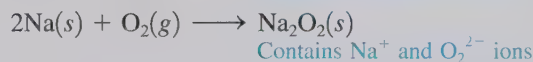
Oxidation–reduction reactions were discussed in Chapter 4.

the melting point of cesium is only 29°C. Cesium can be melted readily using only the heat from your hand. This is very unusual—metals typically have rather high melting points. For example, tungsten melts at 3410°C. The only other metals with low melting points are mercury (mp –38°C) and gallium (mp 30°C).

The chemical property most characteristic of a metal is the ability to lose its valence electrons. The Group 1A elements are very reactive. They have low ionization energies and react with nonmetals to form ionic solids. A typical example involves the reaction of sodium with chlorine to form sodium chloride:



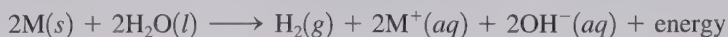
where sodium chloride contains Na^+ and Cl^- ions. This is an oxidation–reduction reaction in which chlorine oxidizes sodium. In the reactions between metals and nonmetals, it is typical for the nonmetal to behave as the oxidizing agent and the metal to behave as the reducing agent, as shown by the following reactions:



For reactions of the types just shown, the relative reducing powers of the alkali metals can be predicted from the first ionization energies listed in Table 7.8. Since it is much easier to remove an electron from a cesium atom than from a lithium atom, cesium should be the better reducing agent. The expected trend in reducing ability is



This order is observed experimentally for direct reactions between the solid alkali metals and nonmetals. However, this is not the order for reducing ability found when the alkali metals react in aqueous solution. For example, the reduction of water by an alkali metal is very vigorous and exothermic:

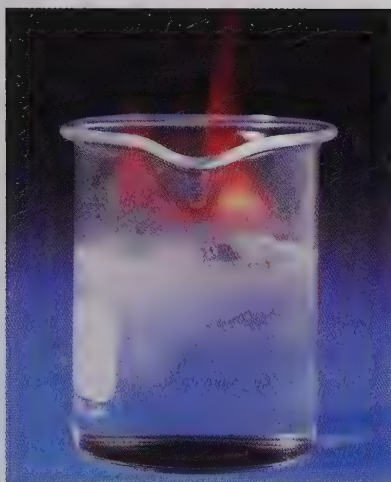


The order of reducing abilities observed for this reaction for the first three group members is



In the gas phase potassium loses an electron more easily than sodium, and sodium more easily than lithium. Thus it is surprising that lithium is the best reducing agent toward water.

This reversal occurs because the formation of the M^+ ions in aqueous solution is strongly influenced by the hydration of these ions by the polar water molecules. The *hydration energy* of an ion represents the change in energy that occurs when water molecules attach to the M^+ ion. The hydration energies for the Li^+ , Na^+ , and K^+ ions (shown in Table 7.9) indicate that the process is exothermic in each case. However, nearly twice as much energy is released by the hydration of the Li^+ ion as for the K^+ ion. This difference is caused by size effects; the Li^+ ion is much smaller than the K^+ ion, and thus its *charge density* (charge per unit volume) is also much greater. This means that the polar water molecules are more strongly attracted



Potassium reacts violently with water.

TABLE 7.9 Hydration Energies for Li^+ , Na^+ , and K^+ Ions

Ion	Hydration Energy (kJ/mol)
Li^+	–510
Na^+	–402
K^+	–314

Potassium—Too Much of a Good Thing Can Kill You

Potassium is widely recognized as an essential element. In fact, our daily requirement for potassium is more than twice that for sodium. Because most foods contain potassium, serious deficiency of this element in humans is rare. However, potassium deficiency can be caused by kidney malfunction or by the use of certain diuretics. Potassium deficiency leads to muscle weakness, irregular heartbeat, and depression.

Potassium is found in the fluids of the body as the K^+ ion, and its presence is essential to the operation of our nervous system. The passage of impulses along the nerves requires the flow of K^+ (and Na^+) through channels in the membranes of the nerve cells. Failure of this ion flow prevents nerve transmissions and results in death. For example, the black mamba snake kills its victims by injecting a venom that blocks the potassium channels in the nerve cells.

Although a steady intake of potassium is essential to preserve life, ironically, too much potassium can be lethal. In fact, the deadly ingredient in the drug mixture used for executing criminals is potassium chloride. Injection of a large amount of a potassium chloride solution produces an excess of K^+ ion in the fluids surrounding the cells and pre-



The black mamba snake's venom kills by blocking the potassium channels in the nerve cells of victims.

vents the essential flow of K^+ out the cells to allow nerve impulses to occur. This causes the heart to stop beating. Unlike other forms of execution, death by lethal injection of potassium chloride does not harm the organs of the body. Thus condemned criminals who are executed in this manner could potentially donate their organs for transplants. However, this idea is very controversial.

to the small Li^+ ion. Because the Li^+ ion is so strongly hydrated, its formation from the lithium atom occurs more readily than the formation of the K^+ ion from the potassium atom. Although a potassium atom in the gas phase loses its valence electron more readily than a lithium atom in the gas phase, the opposite is true in aqueous solution. This anomaly is an example of the importance of the polarity of the water molecule in aqueous reactions.

There is one more surprise involving the highly exothermic reactions of the alkali metals with water. Experiments show that in water lithium is the best reducing agent, so we might expect that lithium should react the most violently with water. However, this is not true. Sodium and potassium react much more vigor-

Key Terms

Section 7.1

electromagnetic radiation
wavelength
frequency

Section 7.2

Planck's constant
quantization
photon
 $E = mc^2$

dual nature of light
diffraction
diffraction pattern

Section 7.3

continuous spectrum
line spectrum

Section 7.4

quantum model
ground state

Section 7.5

standing wave
wave function
orbital
quantum (wave) mechanical model
Heisenberg uncertainty principle
probability distribution
radial probability distribution

Section 7.6

quantum numbers
principal quantum number (n)
angular momentum quantum number (ℓ)
magnetic quantum number (m_ℓ)
subshell

Section 7.7

nodal surface
node
degenerate

Section 7.8

electron spin
electron spin quantum number
Pauli exclusion principle

Section 7.9

polyelectronic atoms

Section 7.11

aufbau principle
Hund's rule
valence electrons
core electrons
transition metals

ously. Why is this so? The answer lies in the relatively high melting point of lithium. When sodium and potassium react with water, the heat evolved causes them to melt, giving a larger area of contact with water. Lithium, on the other hand, does not melt under these conditions and reacts more slowly. This illustrates the important principle (which we will discuss in detail in Chapter 12) that the energy change for a reaction and the rate at which it occurs are not necessarily related.

In this section we have seen that the trends in atomic properties summarized by the periodic table can be a great help in understanding the chemical behavior of the elements. This fact will be emphasized over and over as we proceed in our study of chemistry.

For Review

Summary

Energy can travel through space as electromagnetic radiation, which is characterized by wavelength (λ), frequency (ν), and speed ($c = 2.9979 \times 10^8$ m/s). These three properties are related by the equation $\lambda\nu = c$. Originally, energy was assumed to be continuous, but Planck showed that energy could be lost or gained only in quanta, which are whole-number multiples of $h\nu$ (h is Planck's constant, 6.626×10^{-34} J · s). Einstein postulated that electromagnetic radiation itself can be viewed as a stream of particles called photons, each with energy $h\nu$. Electromagnetic radiation therefore exhibits both wave and particulate properties. The postulate by de Broglie that particles possess wave characteristics was verified by diffraction experiments showing that all matter exhibits the same properties.

A continuous spectrum results from dispersing white light. However, when the emission spectrum produced by excited hydrogen atoms is dispersed, only selected wavelengths are seen, giving a line spectrum. This shows that only certain energies are allowed for the electron in the hydrogen atom.

The Bohr model of the hydrogen atom speculated that the electron in a hydrogen atom moves around the nucleus in certain allowed circular orbits and that the line spectrum was produced when an electron moved from one orbit to another. The Bohr model, however, was shown to be incorrect.

The quantum (wave) mechanical model for the hydrogen atom employs the concept of standing waves. The electron is described by a wave function, often called an orbital, which does not give the exact position for the electron at a given time. This is consistent with the Heisenberg uncertainty principle, which states that it is impossible to know both the position and the momentum of a particle accurately at a given time. However, we can give a physical meaning to the wave function: the square of the function is related to the probability of finding an electron near a particular point in space. Probability distribution (electron density maps) are used to define orbital shapes. Orbitals are characterized by the quantum numbers n , ℓ , and m_ℓ .

Another property of the electron is its spin. An electron appears to spin in two directions, giving rise to two values for the electron spin quantum number (m_s). This concept leads to the Pauli exclusion principle: No two electrons in a given atom can have the same set of four quantum numbers.

lanthanide series
actinide series
main-group elements (representative elements)

Section 7.12

first ionization energy
second ionization energy
electron affinity
atomic radii

Section 7.13

metalloids (semimetals)

Using this principle along with the quantum mechanical model, we can predict the electronic configurations of the atoms in the periodic table. As protons are added one by one to the nucleus to build up the elements, electrons are added to the orbitals. This is called the aufbau principle.

The greatest triumph of the quantum mechanical model is its use to explain the observed periodic properties of the elements as summarized by the periodic table. The chemical properties of an atom are determined by the arrangement of the valence electrons (the electrons in the outermost principal quantum level). Elements in the same group of the periodic table have the same valence electron configurations, which explains why group members show similar chemical properties.

The periodic trends in atomic properties such as ionization energy, electron affinity, and atomic radius can be explained in terms of the concepts of nuclear attraction, electron repulsions, shielding, and penetration.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. What does it mean for something to have wavelike properties? particulate properties? Electromagnetic radiation can be discussed in terms of both particles and waves. Explain the experimental verification for each of these views.
2. Defend and criticize Bohr's model. Why was it reasonable that such a model was proposed, and what evidence was there that it "works"? Why do we no longer "believe" in it?
3. The first four ionization energies for the elements *X* and *Y* are shown below. The units are not kJ/mol.

	<i>X</i>	<i>Y</i>
First	170	200
Second	350	400
Third	1800	3500
Fourth	2500	5000

Identify the elements *X* and *Y*. There may be more than one correct answer, so explain completely.

4. Compare the first ionization energy of helium to its second ionization energy, remembering that both electrons come from the 1s orbital. Explain the difference without using actual numbers from the text.
5. Which has the larger second ionization energy, lithium or beryllium? Why?
6. Explain why a graph of ionization energy versus atomic number (across a row) is not linear. Where are the exceptions? Why are there exceptions?
7. Without referring to your text, predict the trend of second ionization energies for the elements sodium through argon. Compare your answer with Table 7.5. Explain any differences.

8. Account for the fact that the line that separates the metals from the nonmetals on the periodic table is diagonal downward to the right instead of horizontal or vertical.
9. Explain *electron* from a quantum mechanical perspective, including a discussion of atomic radii, probabilities, and orbitals.
10. Choose the best response for the following. The ionization energy for the chlorine atom is equal in magnitude to the electron affinity for
 - a. the Cl atom.
 - b. the Cl⁻ ion.
 - c. the Cl⁺ ion.
 - d. the F atom.
 - e. none of these.

Explain each choice. Justify your choice, and for the choices you did not select, explain what is incorrect about them.

11. Consider the following statement: "The ionization energy for the potassium atom is negative, because when K loses an electron to become K⁺, it achieves a noble gas electron configuration." Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect information and explain.
12. In going across a row of the periodic table, electrons are added and ionization energy generally increases. In going down a column of the periodic table, electrons are also being added but ionization energy decreases. Explain.
13. How does probability fit into the description of the atom?
14. What is meant by an *orbital*?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

Questions

15. What experimental evidence supports the quantum theory for light?

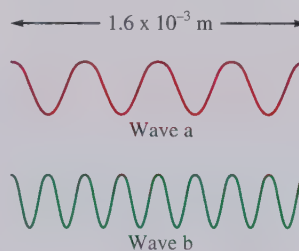
16. What do we mean when we say that something is quantized? In the Bohr model of the hydrogen atom, what is quantized?
17. For what sizes of particles must one consider both wave and particle properties? Summarize some of the evidence supporting the wave properties of matter.
18. Define each of the following terms.
 - a. photon
 - b. quantum number
 - c. ground state
 - d. excited state
19. In the hydrogen atom, what information do we get from the values of the quantum numbers n , ℓ , and m_ℓ ?
20. How do the $2p$ orbitals differ from each other? How do the $2p$ and $3p$ orbitals differ from each other?
21. What is a nodal surface in an atomic orbital?
22. Why can we not account exactly for the repulsions among electrons in a polyelectronic atom?
23. We define a spin quantum number, but do we know that an electron literally spins?
24. Explain what we mean when we say that a $4s$ electron is more penetrating than a $3d$ electron.
25. Why do we emphasize the valence electrons in an atom when discussing atomic properties? What is the relationship between valence electrons and elements in the same group of the periodic table?
26. Many times the claim is made that subshells half-filled with electrons are particularly stable. Can you suggest a possible physical basis for this claim?
27. Explain why the first ionization energy tends to increase as one proceeds from left to right across a period. Why is the first ionization energy of aluminum lower than that of magnesium and the first ionization energy of sulfur lower than that of phosphorus?
28. Why do the successive ionization energies of an atom always increase? Note the successive ionization energies for silicon given in Table 7.5. Would you expect to see any large jumps between successive ionization energies of silicon as you removed all the electrons, one by one, beyond those shown in the table?
29. Using the element phosphorus as an example, write the equation for a process in which the energy change will correspond to the ionization energy and to the electron affinity.
30. Diagonal relationships in the periodic table exist as well as the vertical relationships. For example, Be and Al are similar in some of their properties, as are B and Si. Rationalize why these diagonal relationships hold for properties such as size, ionization energy, and electron affinity.
31. Elements with very large ionization energies also tend to have highly exothermic electron affinities. Explain. Which group of elements would you expect to be an exception to this statement?
32. The changes in electron affinity as one goes down a group in the periodic table are not nearly as large as the variations in ionization energies. Why?
33. Why is it much harder to explain the line spectra of polyelectronic atoms and ions than it is to explain the line spectra of hydrogen and hydrogenlike ions?
34. Scientists use emission spectra to confirm the presence of an element in materials of unknown composition. Why is this possible?
35. Does the minimization of electron–electron repulsions correlate with Hund’s rule?
36. In the hydrogen atom, what is the physical significance of the state for which $n = \infty$ and $E = 0$?
37. The work function is the energy required to remove an electron from an atom on the surface of a metal. How does this definition differ from that for ionization energy?
38. Many more anhydrous lithium salts are hygroscopic (readily absorb water) than are those of the other alkali metals. Explain.

Exercises

In this section similar exercises are paired.

Light and Matter

39. The laser in an audio compact disc player uses light with a wavelength of 7.80×10^2 nm. Calculate the frequency of this light.
40. An FM radio station broadcasts at 99.5 MHz. Calculate the wavelength of the corresponding radio waves.
41. Microwave radiation has a wavelength on the order of 1.0 cm. Calculate the frequency and the energy of a single photon of this radiation. Calculate the energy of an Avogadro’s number of photons (called an *einstein*) of this radiation.
42. A photon of ultraviolet (UV) light possesses enough energy to mutate a strand of human DNA. What is the energy of a single UV photon and a mole of UV photons having a wavelength of 25 nm?
43. Consider the following waves representing electromagnetic radiation:



Which wave has the longer wavelength? Calculate the wavelength. Which wave has the higher frequency and larger

photon energy? Calculate these values. Which wave has the faster velocity? What type of electromagnetic radiation are illustrated?

44. One type of electromagnetic radiation has a frequency of 107.1 MHz, another type has a wavelength of 2.12×10^{-10} m, and another type of electromagnetic radiation has photons with energy equal to 3.97×10^{-19} J/photon. Identify each type of electromagnetic radiation and place them in order of increasing photon energy and increasing frequency.
45. The work function of an element is the energy required to remove an electron from the surface of the solid element. The work function for lithium is 279.7 kJ/mol (that is, it takes 279.7 kJ of energy to remove one mole of electrons from one mole of Li atoms on the surface of Li metal). What is the maximum wavelength of light that can remove an electron from an atom on the surface of lithium metal?
46. It takes 208.4 kJ of energy to remove 1 mole of electrons from an atom on the surface of rubidium metal. How much energy does it take to remove a single electron from an atom on the surface of solid rubidium? What is the maximum wavelength of light capable of doing this?
47. Calculate the de Broglie wavelength for each of the following.
- a proton with a velocity 90.% of the speed of light
 - a 150-g ball with a velocity of 10. m/s
48. Neutron diffraction is used in determining the structures of molecules.
- Calculate the de Broglie wavelength of a neutron moving at 1.00% of the speed of light.
 - Calculate the velocity of a neutron with a wavelength of 75 pm ($1 \text{ pm} = 10^{-12} \text{ m}$).
49. Calculate the de Broglie wavelength of an electron moving with a velocity that is 1.0×10^{-3} times the speed of light.
50. Calculate the velocities of electrons with de Broglie wavelengths of $1.0 \times 10^2 \text{ nm}$ and 1.0 nm, respectively.

Hydrogen Atom: The Bohr Model

51. Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
- $n = 3 \rightarrow n = 2$
 - $n = 4 \rightarrow n = 2$
 - $n = 2 \rightarrow n = 1$
52. Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
- $n = 4 \rightarrow n = 3$
 - $n = 5 \rightarrow n = 4$
 - $n = 5 \rightarrow n = 3$
53. Using vertical lines, indicate the transitions from Exercise 51 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).

54. Using vertical lines, indicate the transitions from Exercise 52 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).
55. Does a photon of visible light ($\lambda \approx 400$ to 700 nm) have sufficient energy to excite an electron in a hydrogen atom from the $n = 1$ to the $n = 5$ energy state? from the $n = 2$ to the $n = 6$ energy state?
56. Calculate the maximum wavelength of light capable of removing an electron from a hydrogen atom from the energy state characterized by $n = 1$, by $n = 2$.
57. An excited hydrogen atom emits light with a frequency of $1.141 \times 10^{14} \text{ Hz}$ to reach the energy level for which $n = 4$. In what principal quantum level did the electron begin?
58. An excited hydrogen atom emits light with a wavelength of 397.2 nm to reach the energy level for which $n = 2$. In which principal quantum level did the electron begin?

Quantum Mechanics, Quantum Numbers, and Orbitals

59. Using the Heisenberg uncertainty principle, calculate Δx for each of the following.
- an electron with $\Delta v = 0.100 \text{ m/s}$
 - a baseball (mass = 145 g) with $\Delta v = 0.100 \text{ m/s}$
 - How does the answer in part a compare with the size of a hydrogen atom?
 - How does the answer in part b correspond to the size of a baseball?
60. The Heisenberg uncertainty principle can be expressed in the form

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

where E represents energy and t represents time. Show that the units for this form are the same as the units for the form used in this chapter:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

61. What are the possible values for the quantum numbers n , ℓ , and m_ℓ ?
62. Which of the following orbital designations are incorrect: 1s, 1p, 7d, 9s, 3f, 4f, 2d?
63. Which of the following sets of quantum numbers are not allowed in the hydrogen atom? For the sets of quantum numbers that are incorrect, state what is wrong in each set.
- $n = 2, \ell = 1, m_\ell = -1$
 - $n = 1, \ell = 1, m_\ell = 0$
 - $n = 8, \ell = 7, m_\ell = -6$
 - $n = 1, \ell = 0, m_\ell = 2$
64. Which of the following sets of quantum numbers are not allowed in the hydrogen atom? For the sets of quantum numbers that are incorrect, state what is wrong in each set.
- $n = 3, \ell = 2, m_\ell = 2$
 - $n = 4, \ell = 3, m_\ell = 4$

- c. $n = 0, \ell = 0, m_\ell = 0$
 d. $n = 2, \ell = -1, m_\ell = 1$

65. What is the physical significance of the value of ψ^2 at a particular point in an atomic orbital?
 66. In defining the sizes of orbitals, why must we use an arbitrary value, such as 90% of the probability of finding an electron in that region?

Polyelectronic Atoms

67. How many orbitals in an atom can have the designation: $5p, 3d_{z^2}, 4d, n = 5, n = 4$?
 68. How many electrons in an atom can have the designation $1p, 6d_{x^2-y^2}, 4f, 7p_y, 2s, n = 3$?
 69. Give the maximum number of electrons in an atom that can have these quantum numbers:
 a. $n = 4$
 b. $n = 5, m_\ell = +1$
 c. $n = 5, m_s = +\frac{1}{2}$
 d. $n = 3, \ell = 2$
 e. $n = 2, \ell = 1$
 70. Give the maximum number of electrons in an atom that can have these quantum numbers:
 a. $n = 0, \ell = 0, m_\ell = 0$
 b. $n = 2, \ell = 1, m_\ell = -1, m_s = -\frac{1}{2}$
 c. $n = 3$
 d. $n = 2, \ell = 2$
 e. $n = 1, \ell = 0, m_\ell = 0$
 71. The elements Si, Ga, As, Ge, Al, Cd, S, and Se are all used in the manufacture of various semiconductor devices. Write the expected electron configuration for these atoms.
 72. The elements Cu, O, La, Y, Ba, Tl, and Bi are all found in high-temperature ceramic superconductors. Write the expected electron configuration for these atoms.
 73. Write the expected electron configurations for each of the following atoms: Sc, Fe, P, Cs, Eu, Pt, Xe, Br.
 74. Write the expected electron configurations for each of the following atoms: Cl, As, Sr, W, Pb, Cf.
 75. Using Fig. 7.28, list the elements (ignore the lanthanides and actinides) that have ground-state electron configurations that differ from those we would expect from their positions in the periodic table.
 76. The electron configurations in Fig. 7.28 are for atoms in the gas phase and are determined experimentally. Would you expect the electron configurations to be the same in the solid and liquid states as in the gas phase?
 77. Write the expected ground-state electron configuration for the following.
 a. The element with one unpaired $5p$ electron that forms a covalent compound with fluorine
 b. The (as yet undiscovered) alkaline earth metal after radium

- c. The noble gas with electrons occupying $4f$ orbitals
 d. The first-row transition metal with the most unpaired electrons
 78. Using only the periodic table inside the front cover of the text, write the expected ground-state electron configurations for
 a. the third element in Group 5A.
 b. element number 116.
 c. an element with three unpaired $5d$ electrons.
 d. the halogen with electrons in the $6p$ atomic orbitals.
 79. Give a possible set of values of the four quantum numbers for all the electrons in a boron atom and a nitrogen atom if each is in the ground state.
 80. Give a possible set of values of the four quantum numbers for the $4s$ and $3d$ electrons in titanium.
 81. A certain oxygen atom has the electron configuration $1s^2 2s^2 2p_x^2 2p_y^2$. How many unpaired electrons are present? Is this an excited state of oxygen? In going from this state to the ground state would energy be released or absorbed?
 82. Which of the following electron configurations correspond to an excited state? Identify the atoms and write the ground-state electron configuration where appropriate.
 a. $1s^2 2s^2 3p^1$
 b. $1s^2 2s^2 2p^6$
 c. $1s^2 2s^2 2p^4 3s^1$
 d. $[\text{Ar}] 4s^2 3d^5 4p^1$
 How many unpaired electrons are present in each of these species?

83. One bit of evidence that the quantum mechanical model is "correct" lies in the magnetic properties of matter. Atoms with unpaired electrons are attracted by magnetic fields and thus are said to exhibit *paramagnetism*. The degree to which this effect is observed is directly related to the number of unpaired electrons present in the atom. Consider the ground-state electron configurations for Li, N, Ni, Te, Ba, and Hg. Which of these atoms would be expected to be paramagnetic, and how many unpaired electrons are present in each paramagnetic atom?
 84. How many unpaired electrons are present in each of the following in the ground state: O, O^+ , O^- , Os, Zr, S, F, Ar?

The Periodic Table and Periodic Properties

85. Arrange the following groups of atoms in order of increasing size.
 a. Be, Mg, Ca
 b. Te, I, Xe
 c. Ga, Ge, In
 86. Arrange the following groups of atoms in order of increasing size.
 a. Rb, Na, Be
 b. Sr, Se, Ne
 c. Fe, P, O

87. Arrange the atoms in Exercise 85 in order of increasing first ionization energy.
88. Arrange the atoms in Exercise 86 in order of increasing first ionization energy.

89. In each of the following sets, which atom or ion has the smallest radius?

- Li, Na, K
- P, As
- O^+ , O, O^-
- S, Cl, Kr
- Pd, Ni, Cu

90. In each of the following sets, which atom or ion has the smallest ionization energy?

- Ca, Sr, Ba
- K, Mn, Ga
- N, O, F
- S^{2-} , S, S^{2+}
- Cs, Ge, Ar

91. In 1994 at an American Chemical Society meeting, it was proposed that element 106 be named seaborgium, Sg, in honor of Glenn Seaborg, discoverer of the first transuranium element.

- Write the expected electron configuration for element 106.
- What other element would be most like element 106 in its properties?
- Write the formula for a possible oxide and a possible oxoanion of element 106.

92. Predict some of the properties of element 117 (the symbol is Uus, following conventions proposed by the International Union of Pure and Applied Chemistry, or IUPAC).

- What will be its electron configuration?
- What element will it most resemble chemically?
- What will be the formula of the neutral binary compounds it forms with sodium, magnesium, carbon, and oxygen?
- What oxoanions would you expect Uus to form?

93. The first ionization energies of As and Se are 0.947 and 0.941 MJ/mol, respectively. Rationalize these values in terms of electron configurations.

94. The electron affinities of the elements from aluminum to chlorine are -44 , -120 , -74 , -200.4 , and -384.7 kJ/mol, respectively. Rationalize the trend in these values.

95. For each of the following pairs of elements

(C and N) (Ar and Br)

pick the atom with

- more favorable (exothermic) electron affinity.
- higher ionization energy.
- larger size.

96. For each of the following pairs of elements

(Mg and K) (F and Cl)

pick the atom with

- more favorable (exothermic) electron affinity.
- higher ionization energy.
- larger size.

97. Order the atoms in each of the following sets from the least exothermic electron affinity to the most.

- S, Se
- F, Cl, Br, I

98. Order the atoms in each of the following sets from the least exothermic electron affinity to the most.

- N, O, F
- Al, Si, P

99. The electron affinity for sulfur is more exothermic than that for oxygen. Account for this.

100. Which would have the more negative electron affinity, the oxygen atom or the O^- ion? Explain.

101. Use data in this chapter to determine

- the electron affinity of Mg^{2+} .
- the electron affinity of Al^+ .

102. Use data in this chapter to determine

- the ionization energy of Cl^- .
- the ionization energy of Cl.
- the electron affinity of Cl^+ .

Alkali Metals

103. An ionic compound of potassium and oxygen has the empirical formula KO. Would you expect this compound to be potassium(II) oxide or potassium peroxide? Explain.

104. Give the name and formula of each of the binary compounds formed from the following elements.

- Li and N
- Na and Br
- K and S

105. Cesium was discovered in natural mineral waters in 1860 by R. W. Bunsen and G. R. Kirchhoff using the spectroscope they invented in 1859. The name came from the Latin *caesius* ("sky blue") because of the prominent blue line observed for this element at 455.5 nm. Calculate the frequency and energy of a photon of this light.

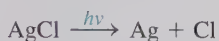
106. The bright yellow light emitted by a sodium vapor lamp consists of two emission lines at 589.0 and 589.6 nm. What are the frequency and the energy of a photon of light at each of these wavelengths? What are the energies in kJ/mol?

107. Does the information on alkali metals in Table 7.8 of the text confirm the general periodic trends in ionization energy and atomic radius? Explain.

108. Predict the atomic number of the next alkali metal after francium and give its ground-state electron configuration.
109. Complete and balance the equations for the following reactions.
- $\text{Li}(s) + \text{O}_2(g) \rightarrow$
 - $\text{K}(s) + \text{S}(s) \rightarrow$
110. Complete and balance the equations for the following reactions.
- $\text{Cs}(s) + \text{H}_2\text{O}(l) \rightarrow$
 - $\text{Na}(s) + \text{Cl}_2(g) \rightarrow$

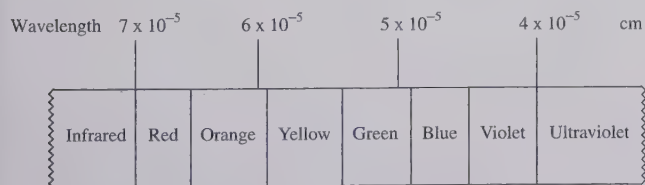
Additional Exercises

111. Photogray lenses incorporate small amounts of silver chloride in the glass of the lens. When light hits the AgCl particles, the following reaction occurs:



The silver metal that is formed causes the lenses to darken. The enthalpy change for this reaction is $3.10 \times 10^2 \text{ kJ/mol}$. Assuming all this energy must be supplied by light, what is the maximum wavelength of light that can cause this reaction?

112. A certain microwave oven delivers 750. watts (joule/s) of power to a coffee cup containing 50.0 g of water at 25.0°C . If the wavelength of microwaves in the oven is 9.75 cm, how long does it take, and how many photons must be absorbed, to make the water boil? The specific heat capacity of water is $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$ and assume only the water absorbs the energy of the microwaves.
113. Mars is roughly 60 million km from earth. How long does it take for a radio signal originating from earth to reach Mars?
114. Consider the following approximate visible light spectrum:

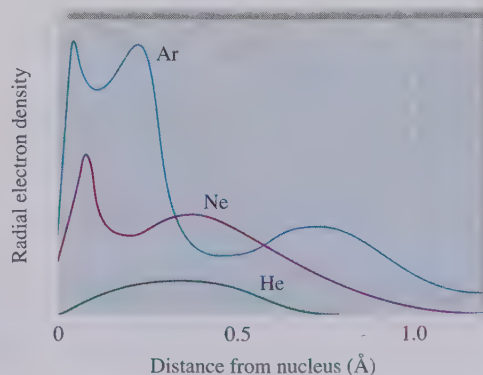


Barium emits light in the visible region of the spectrum. If each photon of light emitted from barium has an energy of $3.90 \times 10^{-19} \text{ J}$, what color of visible light is emitted?

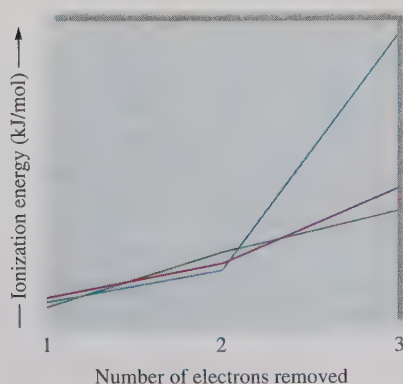
115. One of the visible lines in the hydrogen emission spectrum corresponds to the $n = 6$ to $n = 2$ electronic transition. What color light is this transition? See Exercise 114.
116. An electron is excited from the $n = 1$ ground state to the $n = 3$ state in a hydrogen atom. Which of the following statements are true? Correct the false statements to make them true.

- It takes more energy to ionize the electron from $n = 3$ than from the ground state.
- The electron is farther from the nucleus on average in the $n = 3$ state than in the $n = 1$ state.
- The wavelength of light emitted if the electron drops from $n = 3$ to $n = 2$ will be shorter than the wavelength of light emitted if the electron falls from $n = 3$ to $n = 1$.
- The wavelength of light emitted when the electron returns to the ground state from $n = 3$ will be the same as the wavelength of light absorbed to go from $n = 1$ to $n = 3$.
- For $n = 3$, the electron is in the first excited state.

117. Are the following statements true for the hydrogen atom only, true for all atoms, or not true for any atoms?
- The principal quantum number completely determines the energy of a given electron.
 - The angular momentum quantum number, ℓ , determines the shapes of the atomic orbitals.
 - The magnetic quantum number, m_ℓ , determines the direction that the atomic orbitals point in space.
118. Although no currently known elements contain electrons in g orbitals in the ground state, it is possible that these elements will be found or that electrons in excited states of known elements could be in g orbitals. For g orbitals, the value of ℓ is 4. What is the lowest value of n for which g orbitals could exist? What are the possible values of m_ℓ ? How many electrons could a set of g orbitals hold?
119. In the ground state of cadmium, Cd,
- how many electrons have $\ell = 2$ as one of their quantum numbers?
 - how many electrons have $n = 4$ as one of their quantum numbers?
 - how many electrons have $m_\ell = -1$ as one of their quantum numbers?
 - how many electrons have $m_s = -\frac{1}{2}$ as one of their quantum numbers?
120. Total radial probability distributions for the helium, neon, and argon atoms are shown in the following graph. How can one interpret the shapes of these curves in terms of electron configurations, quantum numbers, and nuclear charges?



121. The following graph plots the first, second, and third ionization energies for Mg, Al, and Si.



Without referencing the text, which plot corresponds to which element? In one of the plots, there is a huge jump in energy between I_2 and I_3 , unlike in the other two plots. Explain this phenomenon.

122. An ion having a 4+ charge and a mass of 49.9 amu has 2 electrons with principal quantum number $n = 1$, 8 electrons with $n = 2$, and 10 electrons with $n = 3$. Supply as many of the properties for the ion as possible from the information given. *Hint:* In forming ions for this species, the 4s electrons are lost before the 3d electrons.

- the atomic number
- total number of s electrons
- total number of p electrons
- total number of d electrons
- the number of neutrons in the nucleus
- the ground-state electron configuration of the neutral atom

123. The successive ionization energies for an unknown element are

$$\begin{aligned} I_1 &= 896 \text{ kJ/mol} \\ I_2 &= 1752 \text{ kJ/mol} \\ I_3 &= 14,807 \text{ kJ/mol} \\ I_4 &= 17,948 \text{ kJ/mol} \end{aligned}$$

To which family in the periodic table does the unknown element most likely belong?

124. An unknown element is a nonmetal and has a valence electron configuration of ns^2np^4 .

- How many valence electrons does this element have?
- What are some possible identities for this element?
- What is the formula of the compound this element would form with potassium?
- Would this element have a larger or smaller radius than barium?
- Would this element have a greater or smaller ionization energy than fluorine?

125. Using data from this chapter, calculate the change in energy expected for each of the following processes.

- $\text{Na}(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)$
- $\text{Mg}(g) + \text{F}(g) \rightarrow \text{Mg}^+(g) + \text{F}^-(g)$
- $\text{Mg}^+(g) + \text{F}(g) \rightarrow \text{Mg}^{2+}(g) + \text{F}^-(g)$
- $\text{Mg}(g) + 2\text{F}(g) \rightarrow \text{Mg}^{2+}(g) + 2\text{F}^-(g)$

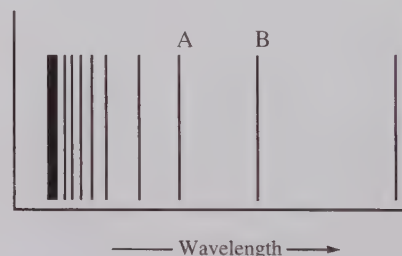
126. Write equations corresponding to the following.

- The fourth ionization energy of Se
- The electron affinity of S^-
- The electron affinity of Fe^{3+}
- The ionization energy of Mg

Challenge Problems

127. One of the emission spectral lines for Be^{3+} has a wavelength of 253.4 nm for an electronic transition that begins in the state with $n = 5$. What is the principal quantum number of the lower-energy state corresponding to this emission? (*Hint:* The Bohr model can be applied to one-electron ions. Don't forget the Z factor: Z = nuclear charge = atomic number.)

128. The figure below represents part of the emission spectrum for a one-electron ion in the gas phase. All the lines result from electronic transitions from excited states to the $n = 3$ state. (See Exercise 127.)



- What electronic transitions correspond to lines A and B?
- If the wavelength of line B is 142.5 nm, calculate the wavelength of line A.

129. The wave function for the $2p_z$ orbital in the hydrogen atom is

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$$

where a_0 is the value for the radius of the first Bohr orbit in meters (5.29×10^{-11}), σ is $Z(r/a_0)$, r is the value for the distance from the nucleus in meters, and θ is an angle. Calculate the value of $\psi_{2p_z}^2$ at $r = a_0$ for $\theta = 0$ (z axis) and for $\theta = 90^\circ$ (xy plane).

130. Answer the following questions assuming that m_e could have three values rather than two and that the rules for n , ℓ , and m_ℓ are the normal ones.

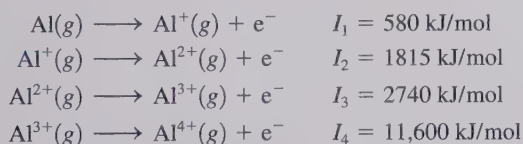
- How many electrons would an orbital be able to hold?
- How many elements would the first and second periods in the periodic table contain?
- How many elements would be contained in the first transition metal series?

- d. How many electrons would the set of $4f$ orbitals be able to hold?
131. Assume that we are in another universe with different physical laws. Electrons in this universe are described by four quantum numbers with meanings similar to those we use. We will call these quantum numbers p , q , r , and s . The rules for these quantum numbers are as follows:
- $p = 1, 2, 3, 4, 5, \dots$
 q takes on positive odd integer values and $q \leq p$.
 r takes on all even integer values from $-q$ to $+q$. (Zero is considered an even number.)
 $s = +\frac{1}{2}$ or $-\frac{1}{2}$
- Sketch what the first four periods of the periodic table will look like in this universe.
 - What are the atomic numbers of the first four elements you would expect to be least reactive?
 - Give an example, using elements in the first four rows, of ionic compounds with the formulas XY , XY_2 , X_2Y , XY_3 , and X_2Y_3 .
 - How many electrons can have $p = 4$, $q = 3$?
 - How many electrons can have $p = 3$, $q = 0$, $r = 0$?
 - How many electrons can have $p = 6$?
132. We expect the atomic radius to increase going down a group in the periodic table. Can you suggest why the atomic radius of hafnium breaks this rule? (See data below.)

Atomic Radii, in pm

Sc	157	Ti	147.7
Y	169.3	Zr	159.3
La	191.5	Hf	147.6

133. Consider the following ionization energies for aluminum:



- Account for the trend in the values of the ionization energies.
 - Explain the large increase between I_3 and I_4 .
 - Which one of the four ions has the greatest electron affinity? Explain.
 - List the four aluminum ions given in order of increasing size, and explain your ordering. (*Hint*: Remember that most of the size of an atom or ion is due to its electrons.)
134. While Mendeleev predicted the existence of several undiscovered elements, he did not predict the existence of the noble gases, the lanthanides, or the actinides. Propose reasons why Mendeleev was not able to predict the existence of the noble gases.

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

135. From the information below, identify element X.
- The wavelength of the radio waves sent by an FM station broadcasting at 97.1 MHz is 30 million (3.00×10^7) times greater than the wavelength corresponding to the energy difference between a particular excited state of the hydrogen atom and the ground state.
 - Let V represent the principal quantum number for the valence shell of element X. If an electron in the hydrogen atom falls from shell V to the inner shell corresponding to the excited state mentioned above in part a, the wavelength of light emitted is the same as the wavelength of an electron moving at a speed of 570. m/s.
 - The number of unpaired electrons for element X in the ground state is the same as the maximum number of electrons in an atom that can have the quantum number designations $n = 2$, $m_l = -1$, and $m_s = -\frac{1}{2}$.
 - Let A equal the charge of the stable ion that would form when the undiscovered element 120 forms ionic compounds. This value of A also represents the angular momentum quantum number for the subshell containing the unpaired electron(s) for element X.



Media Activities

- Play the Electromagnetic Wave Visualization on the student CD. Are wavelength and frequency directly or inversely related? Next, view the Refraction of White Light Visualization to see the visible region of electromagnetic radiation. Does red light have a longer or shorter wavelength than violet light? Does yellow light have a lower or higher frequency than blue light? Which color of light travels at the faster speed? Review Figure 7.2 in the text to help answer these questions.
 - The energy of electromagnetic radiation is transferred in units called photons, as proposed by Albert Einstein. Open the Photoelectric Effect (Yellow or Blue) Visualization on the student CD to view the experiment whose results led Einstein to propose the idea of photons. Is the energy of a photon of light directly or inversely related to wavelength?

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Which color light, yellow or blue, represents the higher frequency light? Higher energy light? Longer wavelength light?

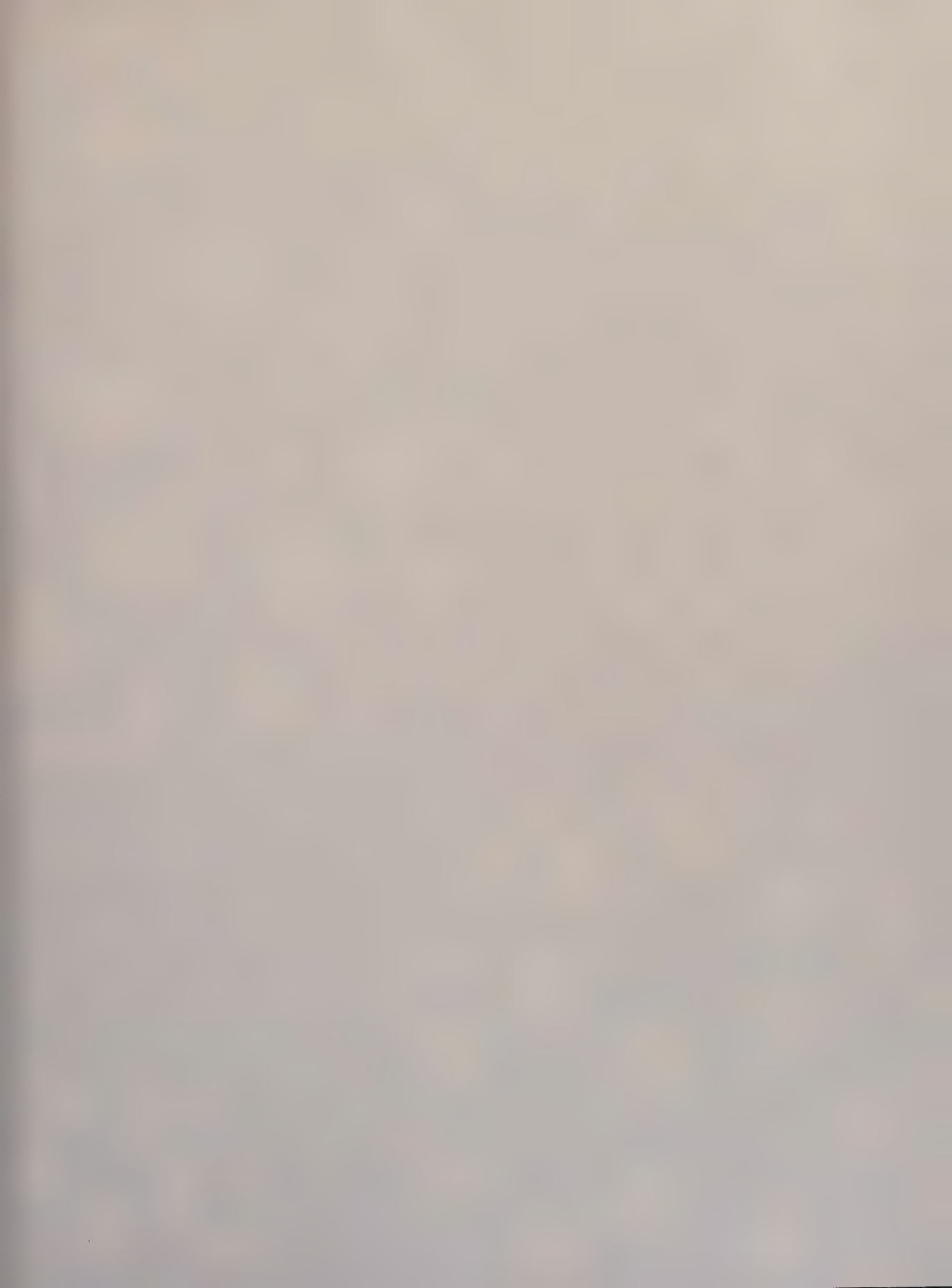
- c. The other types of electromagnetic radiation (in order of increasing wavelength) are gamma rays, X rays, ultraviolet, visible, infrared, microwaves, and radiowaves. Which is the most energetic type of electromagnetic radiation? Which type of electromagnetic radiation travels at the slowest speed: microwaves or visible light?
2. The great success of the Bohr model was its ability to predict the exact wavelengths of light emitted for the hydrogen emission spectrum. Play the Refraction of White Light and the H₂ Line Spectrum Visualizations.
 - a. Using the Bohr model, why aren't all wavelengths of visible light emitted in the H₂ spectrum? Which line in the hydrogen emission spectrum is of highest energy?
 - b. The four lines in the hydrogen emission spectrum correspond to the $n = 6$ to $n = 2$, $n = 5$ to $n = 2$, $n = 4$ to $n = 2$, and $n = 3$ to $n = 2$ electronic transitions in the Bohr model. Match the electronic transitions to the wavelengths listed in the H₂ Line Spectrum Visualization. Verify that

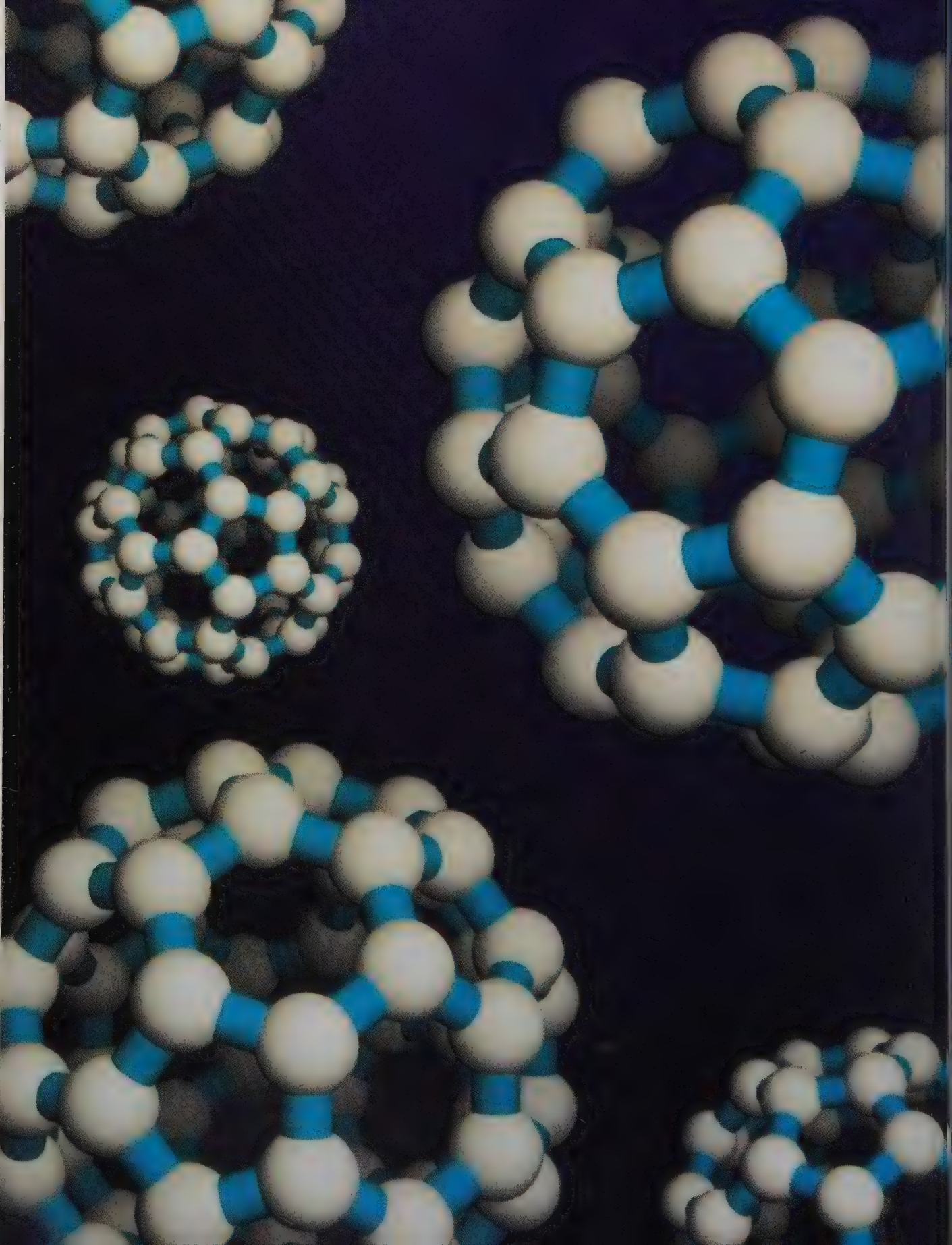
these four electronic transitions produce emissions at the four wavelengths listed in the visualization.

3. View the Flame Tests Visualization. Each salt tested gives off a very distinctive color of light when burned. Explain why we see the flame turn a different color when the various salts are burned. Where is the light coming from? What is the purpose of the flame? Why do the various salts give off different colors of light when burned?
4. The shape of an orbital represents with 90% probability where the electron can be in that specific orbital. Why can't one be 100% sure where the electron is in a specific orbital? Describe the shapes and orientation of the *s*, *p*, and *d* orbitals. Check your answers by viewing the CD Visualizations on the various *s*, *p*, and *d* orbitals.
5. Test your understanding of Chapter 7 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.





Bonding: General Concepts

As we examine the world around us, we find it to be composed almost entirely of compounds and mixtures of compounds: Rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together. Substances composed of unbound atoms do exist in nature, but they are very rare. Examples are the argon in the atmosphere and the helium mixed with natural gas reserves.

The manner in which atoms are bound together has a profound effect on chemical and physical properties. For example, graphite is a soft, slippery material used as a lubricant in locks, and diamond is one of the hardest materials known, valuable both as a gemstone and in industrial cutting tools. Why do these materials, both composed solely of carbon atoms, have such different properties? The answer, as we will see, lies in the bonding in these substances.

Silicon and carbon are next to each other in Group 4A of the periodic table. From our knowledge of periodic trends, we might expect SiO_2 and CO_2 to be very similar. But SiO_2 is the empirical formula of silica, which is found in sand and quartz, and carbon dioxide is a gas, a product of respiration. Why are they so different? We will be able to answer this question after we have developed models for bonding.

Molecular bonding and structure play the central role in determining the course of all chemical reactions, many of which are vital to our survival. Later in this book we will demonstrate their importance by showing how enzymes facilitate complex chemical reactions, how genetic characteristics are transferred, and how hemoglobin in the blood carries oxygen throughout the body. All of these fundamental biological reactions hinge on the geometric structures of molecules, sometimes depending on very subtle differences in molecular shape to channel the chemical reaction one way rather than another.

Carbon forms very stable spherical C_{60} molecules.

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 - Predicting Formulas of Ionic Compounds
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Quartz grows in beautiful, regular crystals.



Many of the world's current problems require fundamentally chemical answers: disease and pollution control, the search for new energy sources, the development of new fertilizers to increase crop yields, the improvement of the protein content in various staple grains, and many more. To understand the behavior of natural materials, we must understand the nature of chemical bonding and the factors that control the structures of compounds. In this chapter we will present various classes of compounds that illustrate the different types of bonds and then develop models to describe the structure and bonding that characterize materials found in nature. Later these models will be useful in understanding chemical reactions.

8.1 *Types of Chemical Bonds*

What is a chemical bond? There is no simple and yet complete answer to this question. In Chapter 2 we defined bonds as forces that hold groups of atoms together and make them function as a unit.

There are many types of experiments we can perform to determine the fundamental nature of materials. For example, we can study physical properties such as melting point, hardness, and electrical and thermal conductivity. We can also study solubility characteristics and the properties of the resulting solutions. To determine the charge distribution in a molecule, we can study its behavior in an electric field. We can obtain information about the strength of a bonding interaction by measuring the **bond energy**, which is the energy required to break the bond.

There are several ways in which atoms can interact with one another to form aggregates. We will consider several specific examples to illustrate the various types of chemical bonds.

Earlier, we saw that when solid sodium chloride is dissolved in water, the resulting solution conducts electricity, a fact that helps to convince us that sodium chloride is composed of Na^+ and Cl^- ions. Therefore, when sodium and chlorine react to form sodium chloride, electrons are transferred from the sodium atoms to the chlorine atoms to form Na^+ and Cl^- ions, which then aggregate to form solid

sodium chloride. Why does this happen? The best simple answer is that *the system can achieve the lowest possible energy by behaving in this way*. The attraction of a chlorine atom for the extra electron and the very strong mutual attractions of the oppositely charged ions provide the driving forces for the process. The resulting solid sodium chloride is a very sturdy material; it has a melting point of approximately 800°C. The bonding forces that produce this great thermal stability result from the electrostatic attractions of the closely packed, oppositely charged ions. This is an example of **ionic bonding**. Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons. That is, an **ionic compound** results when a metal reacts with a nonmetal.

The energy of interaction between a pair of ions can be calculated using **Coulomb's law** in the form

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left(\frac{Q_1 Q_2}{r} \right)$$

where E has units of joules, r is the distance between the ion centers in nanometers, and Q_1 and Q_2 are the numerical ion charges.

For example, in solid sodium chloride the distance between the centers of the Na^+ and Cl^- ions is 2.76 Å (0.276 nm), and the ionic energy per pair of ions is

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left[\frac{(+1)(-1)}{0.276 \text{ nm}} \right] = -8.37 \times 10^{-19} \text{ J}$$

where the negative sign indicates an attractive force. That is, the *ion pair has lower energy than the separated ions*.

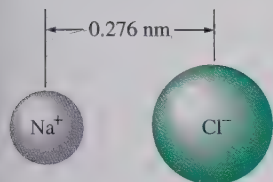
Coulomb's law also can be used to calculate the repulsive energy when two like-charged ions are brought together. In this case the calculated value of the energy will have a positive sign.

We have seen that a bonding force develops when two different types of atoms react to form oppositely charged ions. But how does a bonding force develop between two identical atoms? Let's explore this situation from a very simple point of view by considering the energy terms that result when two hydrogen atoms are brought close together, as shown in Fig. 8.1(a). When hydrogen atoms are brought close together, there are two unfavorable potential energy terms, proton–proton repulsion and electron–electron repulsion, and one favorable term, proton–electron attraction. Under what conditions will the H_2 molecule be favored over the separated hydrogen atoms? That is, what conditions will favor bond formation? The answer lies in the strong tendency in nature for any system to achieve the lowest possible energy. A bond will form (that is, the two hydrogen atoms will exist as a molecular unit) if the system can lower its total energy in the process.

In this case, then, the hydrogen atoms will position themselves so that the system will achieve the lowest possible energy; the system will act to minimize the sum of the positive (repulsive) energy terms and the negative (attractive) energy term. The distance where the energy is minimal is called the **bond length**. The total energy of this system as a function of distance between the hydrogen nuclei is shown in Fig. 8.1(b). Note several important features of this diagram:

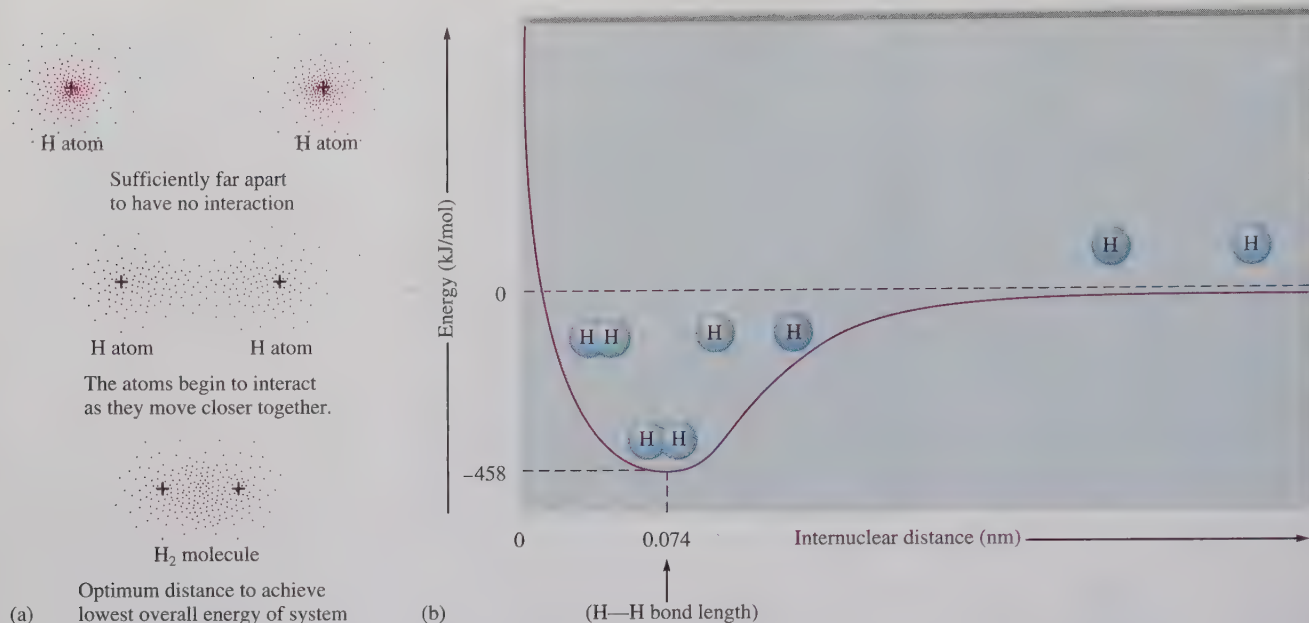
The energy terms involved are the net potential energy that results from the attractions and repulsions among the charged particles and the kinetic energy due to the motions of the electrons.

The zero point of energy is defined with the atoms at infinite separation.



A bond will form if the energy of the aggregate is lower than that of the separated atoms.

Potential energy was discussed in Chapter 6.

**FIGURE 8.1**

(a) The interaction of two hydrogen atoms. (b) Energy profile as a function of the distance between the nuclei of the hydrogen atoms. As the atoms approach each other (right side of graph), the energy decreases until the distance reaches 0.074 nm (0.74 Å) and then begins to increase again due to repulsions.

At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together.

The bond length is the distance at which the system has minimum energy.

In the H₂ molecule, the electrons reside primarily in the space between the two nuclei, where they are attracted simultaneously by both protons. This positioning is precisely what leads to the stability of the H₂ molecule compared with two separated hydrogen atoms. The potential energy of each electron is lowered because of the increased attractive forces in this area. When we say that a bond is formed between the hydrogen atoms, we mean that the H₂ molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy).

We can also think of a bond in terms of forces. The simultaneous attraction of each electron by the protons generates a force that pulls the protons toward each other and that just balances the proton–proton and electron–electron repulsive forces at the distance corresponding to the bond length.

The type of bonding we encounter in the hydrogen molecule and in many other molecules in which *electrons are shared by nuclei* is called **covalent bonding**.

So far we have considered two extreme types of bonding. In ionic bonding the participating atoms are so different that one or more electrons are transferred to form oppositely charged ions, which then attract each other. In covalent bonding two identical atoms share electrons equally. The bonding results from the mutual attraction of the two nuclei for the shared electrons. Between these extremes are intermediate cases in which the atoms are not so different that electrons are completely transferred but are different enough that unequal sharing results, forming

Ionic and covalent bonds are the extreme bond types.

No Lead Pencils

Did you ever wonder why the part of a pencil that makes the mark is called the “lead”? Pencils have no lead in them now—and they never have. Apparently the association between writing and the element lead arose during the Roman Empire, when lead rods were used as writing utensils because they leave a gray mark on paper. Many centuries later, in 1564, a deposit of a black substance found to be very useful for writing was discovered in Borrowdale, England. This substance, originally called “black lead,” was shown in 1879 by Swedish chemist Carl Sheele to be a form of carbon and was subsequently named graphite (after the Greek *graphein*, meaning “to write”).

Originally, chunks of graphite from Borrowdale, called marking stones, were used as writing instruments. Later, sticks of graphite were used. Because graphite is brittle, the sticks needed reinforcement. At first they were wrapped in string, which was unwound as the core wore down. Eventually, graphite rods were tied between two wooden slats or inserted into hollowed-out wooden sticks to form the first crude pencils.

Although Borrowdale graphite was pure enough to use directly, most graphite must be mixed with other materials to be useful for writing instruments. In 1795, the French chemist Nicolas-Jaques Conté invented a process in which graphite is mixed with clay and water to produce pencil “lead,” a recipe that is still used today. In modern pencil manufacture, graphite and clay are mixed and crushed into a fine powder to which water is added. After the gray sludge is blended for several days, it is dried, ground up again, and mixed with more water to give a gray paste. The paste is extruded through a metal tube to form thin rods, which are then cut into pencil-length pieces called “leads.” These leads

are heated in an oven to 1000°C until they are smooth and hard. The ratio of clay to graphite is adjusted to vary the hardness of the lead—the more clay in the mix, the harder the lead and the lighter the line it makes.

Pencils are made from a slat of wood with several grooves cut in it to hold the leads. A similar grooved slat is then placed on top and glued to form a “sandwich” from which individual pencils are cut, sanded smooth, and painted. Although many types of wood have been used over the years to make pencils, the current favorite is incense cedar from the Sierra Nevada Mountains of California.

Modern pencils are simple but amazing instruments. The average pencil can write approximately 45,000 words, which is equivalent to a line 35 miles long. The graphite in a pencil is easily transferred to paper because graphite contains layers of carbon atoms bound together in a “chicken-wire” structure. Although the bonding *within* each layer is very strong, the bonding *between* layers is weak, giving graphite its slippery, soft nature. In this way, graphite is much different from diamond, the other common elemental form of carbon. In diamond the carbon atoms are bound tightly in all three dimensions, making it extremely hard—the hardest natural substance.

Pencils are very useful—especially for doing chemistry problems—because we can erase our mistakes. Most pencils used in the United States have erasers (first attached to pencils in 1858), although most European pencils do not. Laid end-to-end, the number of pencils made in the United States each year would circle the earth about 15 times. Pencils illustrate how useful a simple substance like graphite can be.

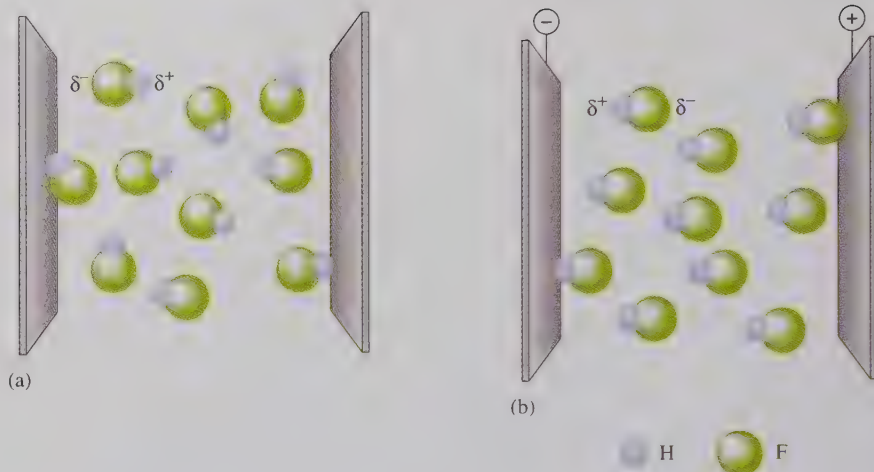
what is called a **polar covalent bond**. An example of this type of bond occurs in the hydrogen fluoride (HF) molecule. When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves as shown in Fig. 8.2, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole. This result implies that the HF molecule has the following charge distribution:



where δ (lowercase delta) is used to indicate a fractional charge. This same effect was noted in Chapter 4, where many of water’s unusual properties were attributed to the polar O—H bonds in the H_2O molecule.

FIGURE 8.2

The effect of an electric field on hydrogen fluoride molecules. (a) When no electric field is present, the molecules are randomly oriented. (b) When the field is turned on, the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.



The most logical explanation for the development of the partial positive and negative charges on the atoms (bond polarity) in such molecules as HF and H_2O is that the electrons in the bonds are not shared equally. For example, we can account for the polarity of the HF molecule by assuming that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom. Likewise, in the H_2O molecule the oxygen atom appears to attract the shared electrons more strongly than the hydrogen atoms do. Because bond polarity has important chemical implications, we find it useful to quantify the ability of an atom to attract shared electrons. In the next section we show how this is done.

8.2 Electronegativity

The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**: *the ability of an atom in a molecule to attract shared electrons to itself.*

The most widely accepted method for determining values of electronegativity is that of Linus Pauling (1901–1995), an American scientist who won the Nobel Prizes for both chemistry and peace. To understand Pauling's model, consider a hypothetical molecule HX. The relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy with the “expected” H—X bond energy, which is an average of the H—H and X—X bond energies:

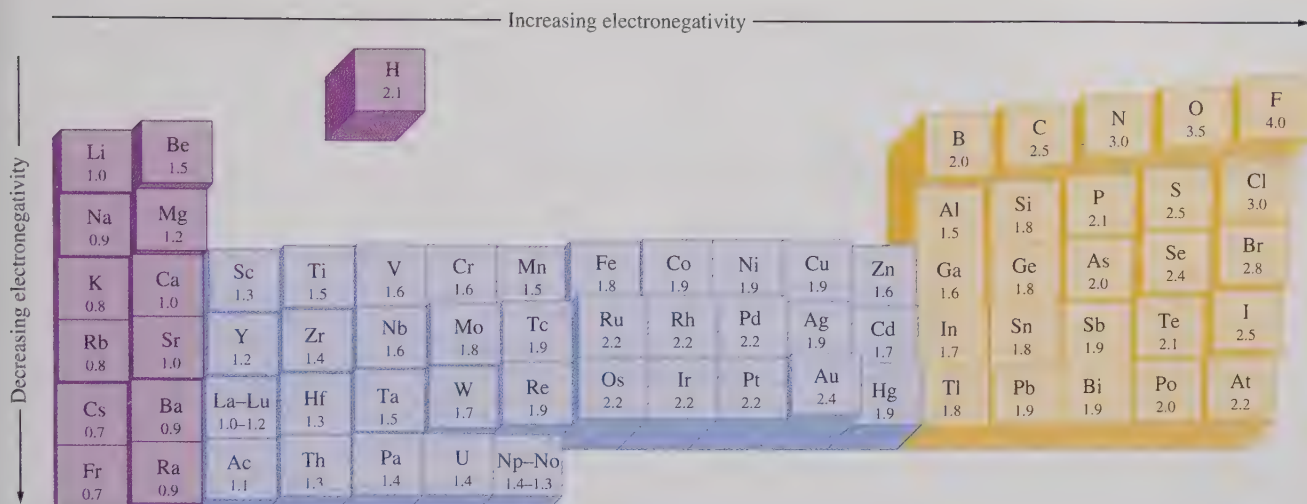
$$\text{Expected H—X bond energy} = \frac{\text{H—H bond energy} + \text{X—X bond energy}}{2}$$

The difference (Δ) between the actual (measured) and expected bond energies is

$$\Delta = (\text{H—X})_{\text{act}} - (\text{H—X})_{\text{exp}}$$

If H and X have identical electronegativities, $(\text{H—X})_{\text{act}}$ and $(\text{H—X})_{\text{exp}}$ are the same, and Δ is 0. On the other hand, if X has a greater electronegativity than H, the shared electron(s) will tend to be closer to the X atom. The molecule will be polar, with the following charge distribution:



**FIGURE 8.3**

The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.

Note that this bond can be viewed as having an ionic as well as a covalent component. The attraction between the partially (and oppositely) charged H and X atoms will lead to a greater bond strength. Thus $(\text{H}-\text{X})_{\text{act}}$ will be larger than $(\text{H}-\text{X})_{\text{exp}}$. The greater is the difference in the electronegativities of the atoms, the greater is the ionic component of the bond and the greater is the value of Δ . Thus the relative electronegativities of H and X can be assigned from the Δ values.

Electronegativity values have been determined by this process for virtually all the elements; the results are given in Fig. 8.3. Note that electronegativity generally increases going from left to right across a period and decreases going down a group for the representative elements. The range of electronegativity values is from 4.0 for fluorine to 0.7 for cesium.

The relationship between electronegativity and bond type is shown in Table 8.1. For identical atoms (an electronegativity difference of zero), the electrons in the bond are shared equally, and no polarity develops. When two atoms with very dif-

TABLE 8.1 The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic

Zero
↓
Intermediate
↓
Large

Covalent
↓
Polar covalent
↓
Ionic

Covalent character ↑

↓ Ionic character

ferent electronegativities interact, electron transfer can occur to form the ions that make up an ionic substance. Intermediate cases give polar covalent bonds with unequal electron sharing.

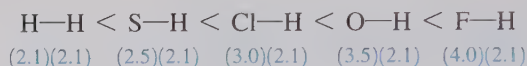
SAMPLE EXERCISE 8.1

Relative Bond Polarities

Order the following bonds according to polarity: H—H, O—H, Cl—H, S—H, and F—H.

SOLUTION

The polarity of the bond increases as the difference in electronegativity increases. From the electronegativity values in Fig. 8.3, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):



Electronegativity
difference

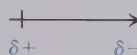
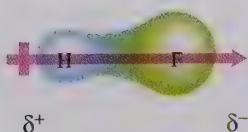
0 0.4 0.9 1.4 1.9

Covalent bond $\longrightarrow$ Polar covalent bond
Polarity increases

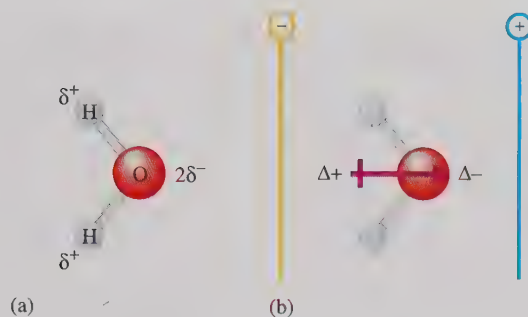
See Exercises 8.27 and 8.28.

8.3 Bond Polarity and Dipole Moments

We have seen that when hydrogen fluoride is placed in an electric field, the molecules have a preferential orientation (see Fig. 8.2). This follows from the charge distribution in the HF molecule, which has a positive end and a negative end. A molecule such as HF that has a center of positive charge and a center of negative charge is said to be **dipolar**, or to have a **dipole moment**. The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge:



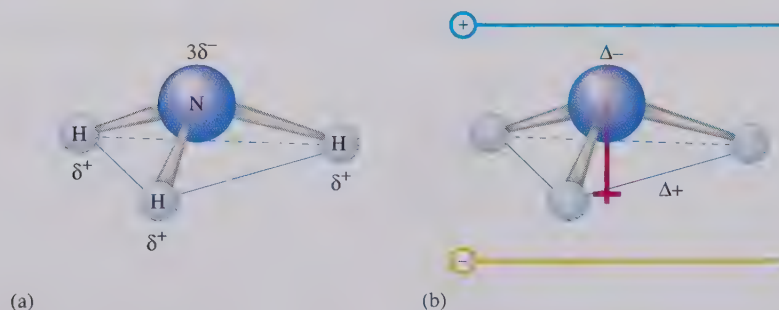
Of course, any diatomic (two-atom) molecule that has a polar bond also will show a molecular dipole moment. Polyatomic molecules also can exhibit dipolar behavior. For example, because the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms, the molecular charge distribution is that shown in Fig. 8.4(a). Because of this charge distribution, the water molecule behaves in an electric field as if it had two centers of charge—one positive and one negative—as shown in Fig. 8.4(b). The water molecule has a dipole moment. The same type of behavior is observed for the NH_3 molecule (Fig. 8.5). Some molecules have polar bonds but do not have a dipole moment. This occurs when the individ-

**FIGURE 8.4**

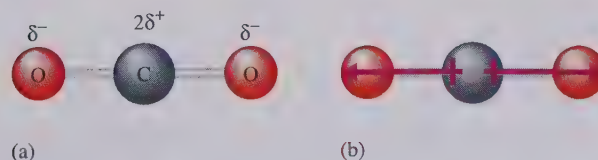
(a) The charge distribution in the water molecule. (b) The water molecule in an electric field.

ual bond polarities are arranged in such a way that they cancel each other out. An example is the CO_2 molecule, which is a linear molecule that has the charge distribution shown in Fig. 8.6. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment. There is no preferential way for this molecule to line up in an electric field. (Try to find a preferred orientation to make sure you understand this concept.)

There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are shown in Table 8.2.

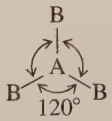
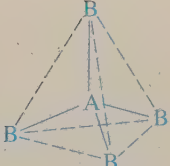
**FIGURE 8.5**

(a) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen. (b) The dipole moment of the ammonia molecule oriented in an electric field.

**FIGURE 8.6**

(a) The carbon dioxide molecule. (b) The opposed bond polarities cancel out, and the carbon dioxide molecule has no dipole moment.

TABLE 8.2 Types of Molecules with Polar Bonds but No Resulting Dipole Moment

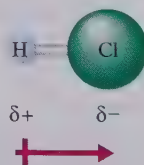
Type		Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	$B-A-B$	$\leftarrow + \quad + \rightarrow$	CO_2	
Planar molecules with three identical bonds 120 degrees apart			SO_3	
Tetrahedral molecules with four identical bonds 109.5 degrees apart			CCl_4	

SAMPLE EXERCISE 8.2**Bond Polarity and Dipole Moment**

For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCl , Cl_2 , SO_3 (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH_4 [tetrahedral (see Table 8.2) with the carbon atom at the center], and H_2S (V-shaped with the sulfur atom at the point).

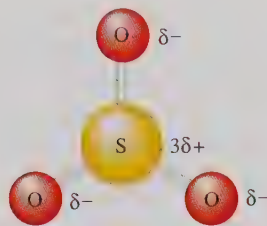
SOLUTION

The HCl molecule: In Fig. 8.3, we see that the electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1). Thus the chlorine will be partially negative, and the hydrogen will be partially positive. The HCl molecule has a dipole moment:



The Cl_2 molecule: The two chlorine atoms share the electrons equally. No bond polarity occurs, and the Cl_2 molecule has no dipole moment.

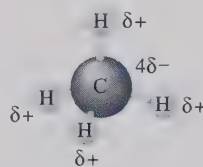
The SO_3 molecule: The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5). This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge:



The presence of polar bonds does not always yield a polar molecule.

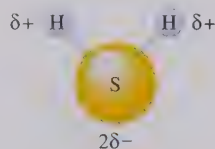
The bond polarities arranged symmetrically as shown cancel, and the molecule has no dipole moment. This molecule is the second type shown in Table 8.2.

The CH_4 molecule: Carbon has a slightly higher electronegativity (2.5) than does hydrogen (2.1). This leads to small partial positive charges on the hydrogen atoms and a small partial negative charge on the carbon:

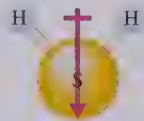


This case is similar to the third type in Table 8.2, and the bond polarities cancel. The molecule has no dipole moment.

The H_2S molecule: Since the electronegativity of sulfur (2.5) is slightly greater than that of hydrogen (2.1), the sulfur will have a partial negative charge, and the hydrogen atoms will have a partial positive charge, which can be represented as



This case is analogous to the water molecule, and the polar bonds result in a dipole moment oriented as shown:



See Question 8.17.

8.4 Ions: Electron Configurations and Sizes

The description of the electron arrangements in atoms that emerged from the quantum mechanical model has helped a great deal in our understanding of what constitutes a stable compound. In virtually every case the atoms in a stable compound

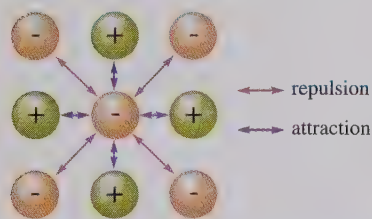
Atoms in stable compounds usually have a noble gas electron configuration.

have a noble gas arrangement of electrons. Nonmetallic elements achieve a noble gas electron configuration either by sharing electrons with other nonmetals to form covalent bonds or by taking electrons from metals to form ions. In the second case, the nonmetals form anions, and the metals form cations. The generalizations that apply to electron configurations in stable compounds are as follows:

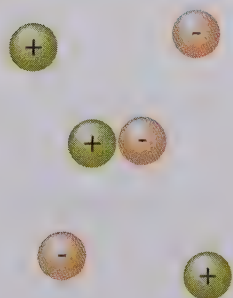
- When *two nonmetals* react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations.
- When *a nonmetal and a representative-group metal* react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied. In this way both ions achieve noble gas electron configurations.

These generalizations apply to the vast majority of compounds and are important to remember. We will deal with covalent bonds more thoroughly later, but now we will consider what implications these rules hold for ionic compounds.

In the solid state of an ionic compound the ions are relatively close together, and many ions are simultaneously interacting:



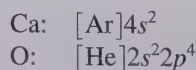
In the gas phase of an ionic substance the ions would be relatively far apart and would not contain large groups of ions:



Predicting Formulas of Ionic Compounds

At the beginning of this discussion it should be emphasized that when chemists use the term *ionic compound*, they are usually referring to the solid state of that compound. In the solid state the ions are close together. That is, solid ionic compounds contain a large collection of positive and negative ions packed together in a way that minimizes the $\ominus \cdots \ominus$ and $\oplus \cdots \oplus$ repulsions and maximizes the $\oplus \cdots \ominus$ attractions. This situation stands in contrast to the gas phase of an ionic substance, where the ions are quite far apart on average. In the gas phase, a pair of ions may get close enough to interact, but large collections of ions do not exist. Thus, when we speak in this text of the stability of an ionic compound, we are referring to the solid state, where the large attractive forces present among oppositely charged ions tend to stabilize (favor the formation of) the ions. For example, as we mentioned in the preceding chapter, the O^{2-} ion is not stable as an isolated, gas-phase species but, of course, is very stable in many solid ionic compounds. That is, MgO(s) , which contains Mg^{2+} and O^{2-} ions, is very stable, but the isolated, gas-phase ion pair $\text{Mg}^{2+} \cdots \text{O}^{2-}$ is not energetically favorable in comparison with the separate neutral gaseous atoms. Thus you should keep in mind that in this section, and in most other cases where we are describing the nature of ionic compounds, the discussion usually refers to the solid state, where many ions are simultaneously interacting.

To illustrate the principles of electron configurations in stable, solid ionic compounds, we will consider the formation of an ionic compound from calcium and oxygen. We can predict what compound will form by considering the valence electron configurations of the two atoms:

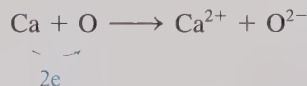


From Fig. 8.3 we see that the electronegativity of oxygen (3.5) is much greater than that of calcium (1.0). Because of this large difference, electrons will be transferred from calcium to oxygen to form oxygen anions and calcium cations in the



Understanding Concepts:
Formation of Ionic Compounds from Ions

compound. How many electrons are transferred? We can base our prediction on the observation that noble gas configurations are generally the most stable. Note that oxygen needs two electrons to fill its $2s$ and $2p$ valence orbitals and to achieve the configuration of neon ($1s^2 2s^2 2p^6$). And by losing two electrons, calcium can achieve the configuration of argon. Two electrons are therefore transferred:



To predict the formula of the ionic compound, we simply recognize that chemical compounds are always electrically neutral—they have the same quantities of positive and negative charges. In this case we have equal numbers of Ca^{2+} and O^{2-} ions, and the empirical formula of the compound is CaO .

The same principles can be applied to many other cases. For example, consider the compound formed between aluminum and oxygen. Because aluminum has the configuration $[\text{Ne}]3s^2 3p^1$, it loses three electrons to form the Al^{3+} ion and thus achieves the neon configuration. Therefore, the Al^{3+} and O^{2-} ions form in this case. Since the compound must be electrically neutral, there must be three O^{2-} ions for every two Al^{3+} ions, and the compound has the empirical formula Al_2O_3 .

Table 8.3 shows common elements that form ions with noble gas electron configurations in ionic compounds. In losing electrons to form cations, metals in Group 1A lose one electron, those in Group 2A lose two electrons, and those in Group 3A lose three electrons. In gaining electrons to form anions, nonmetals in Group 7A (the halogens) gain one electron, and those in Group 6A gain two electrons. Hydrogen typically behaves as a nonmetal and can gain one electron to form the hydride ion (H^-), which has the electron configuration of helium.

There are some important exceptions to the rules discussed here. For example, tin forms both Sn^{2+} and Sn^{4+} ions, and lead forms both Pb^{2+} and Pb^{4+} ions. Also, bismuth forms Bi^{3+} and Bi^{5+} ions, and thallium forms Tl^+ and Tl^{3+} ions. There are no simple explanations for the behavior of these ions. For now, just note them as exceptions to the very useful rule that ions generally adopt noble gas electron



A bauxite mine. Bauxite contains Al_2O_3 , the main source of aluminum.

TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H ⁻ , Li ⁺	Be ²⁺				[He]
Na ⁺	Mg ²⁺	Al ³⁺	O ²⁻	F ⁻	[Ne]
K ⁺	Ca ²⁺		S ²⁻	Cl ⁻	[Ar]
Rb ⁺	Sr ²⁺		Se ²⁻	Br ⁻	[Kr]
Cs ⁺	Ba ²⁺		Te ²⁻	I ⁻	[Xe]

configurations in ionic compounds. Our discussion here refers to representative metals. The transition metals exhibit more complicated behavior, forming a variety of ions that will be considered in Chapter 21.

Sizes of Ions

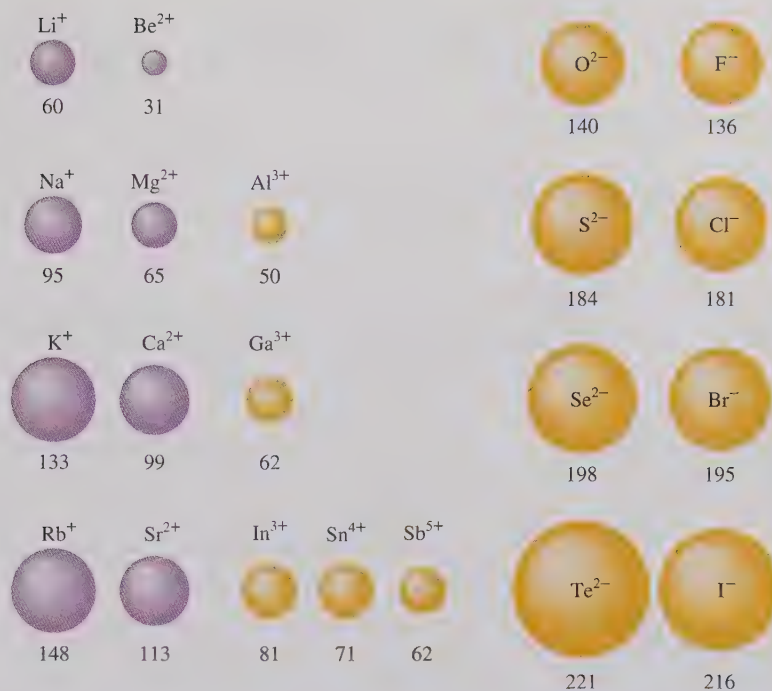
Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biologic effects of ions. As with atoms, it is impossible to define precisely the sizes of ions. Most often, ionic radii are determined from the measured distances between ion centers in ionic compounds. This method, of course, involves an assumption about how the distance should be divided up between the two ions. Thus you will note considerable disagreement among ionic sizes given in various sources. Here we are mainly interested in trends and will be less concerned with absolute ion sizes.

Various factors influence ionic size. We will first consider the relative sizes of an ion and its parent atom. Since a positive ion is formed by removing one or more electrons from a neutral atom, the resulting cation is smaller than its parent atom. The opposite is true for negative ions; the addition of electrons to a neutral atom produces an anion significantly larger than its parent atom.

It is also important to know how the sizes of ions vary depending on the positions of the parent elements in the periodic table. Figure 8.7 shows the sizes of the most important ions (each with a noble gas configuration) and their position in the periodic table. Note that ion size increases down a group. The changes that occur horizontally are complicated because of the change from predominantly metals on the left-hand side of the periodic table to nonmetals on the right-hand side. A given period thus contains both elements that give up electrons to form cations and ones that accept electrons to form anions.

One trend worth noting involves the relative sizes of a set of **isoelectronic ions**—ions containing the same number of electrons. Consider the ions O²⁻, F⁻, Na⁺, Mg²⁺, and Al³⁺. Each of these ions has the neon electron configuration. How do the sizes of these ions vary? In general, there are two important facts to consider in predicting the relative sizes of ions: the number of electrons and the number of protons. Since these ions are isoelectronic, the number of electrons is 10 in each case. Electron repulsions therefore should be about the same in all cases. However, the number of protons increases from 8 to 13 as we go from the O²⁻ ion to the Al³⁺ ion. Thus, in going from O²⁻ to Al³⁺, the 10 electrons experience a greater attraction as the positive charge on the nucleus increases. This causes the ions to become smaller. You can confirm this by looking at Fig. 8.7. In general, for a series of isoelectronic ions, the size decreases as the nuclear charge *Z* increases.

For isoelectronic ions, size decreases as *Z* increases.

**FIGURE 8.7**

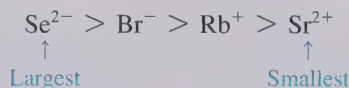
Sizes of ions related to positions of the elements on the periodic table. Note that size generally increases down a group. Also note that in a series of isoelectronic ions, size decreases with increasing atomic number. The ionic radii are given in units of picometers.

SAMPLE EXERCISE 8.3**Relative Ion Size I**

Arrange the ions Se^{2-} , Br^- , Rb^+ , and Sr^{2+} in order of decreasing size.

SOLUTION

This is an isoelectronic series of ions with the krypton electron configuration. Since these ions all have the same number of electrons, their sizes will depend on the nuclear charge. The Z values are 34 for Se^{2-} , 35 for Br^- , 37 for Rb^+ , and 38 for Sr^{2+} . Since the nuclear charge is greatest for Sr^{2+} , it is the smallest of these ions. The Se^{2-} ion is largest:



See Exercises 8.33 and 8.34.

SAMPLE EXERCISE 8.4**Relative Ion Size II**

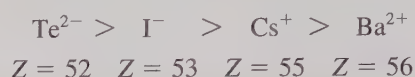
Choose the largest ion in each of the following groups.

- Li^+ , Na^+ , K^+ , Rb^+ , Cs^+
- Ba^{2+} , Cs^+ , I^- , Te^{2-}

SOLUTION

- The ions are all from Group 1A elements. Since size increases down a group (the ion with the greatest number of electrons is largest), Cs^+ is the largest ion.

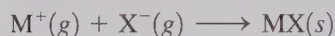
- b. This is an isoelectronic series of ions, all of which have the xenon electron configuration. The ion with the smallest nuclear charge is largest:



See Exercises 8.35 and 8.36.

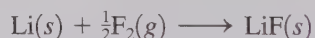
8.5 Energy Effects in Binary Ionic Compounds

In this section we will introduce the factors that influence the stability and the structures of solid binary ionic compounds. We know that metals and nonmetals react by transferring electrons to form cations and anions that are mutually attractive. The resulting ionic solid forms because the aggregated oppositely charged ions have a lower energy than the original elements. Just how strongly the ions attract each other in the solid state is indicated by the **lattice energy**—the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid:



The lattice energy is often defined as the energy *released* when an ionic solid forms from its ions. However, in this book the sign of an energy term is always determined from the system's point of view: negative if the process is exothermic, positive if endothermic. Thus, using this convention, the lattice energy has a negative sign.

We can illustrate the energy changes involved in the formation of an ionic solid by considering the formation of solid lithium fluoride from its elements:



To see the energy terms associated with this process, we take advantage of the fact that energy is a state function and break this reaction into steps, the sum of which gives the overall reaction.

STEP 1 Sublimation of solid lithium. Sublimation involves taking a substance from the solid state to the gaseous state:



The enthalpy of sublimation for Li(s) is 161 kJ/mol.

STEP 2 Ionization of lithium atoms to form Li⁺ ions in the gas phase:



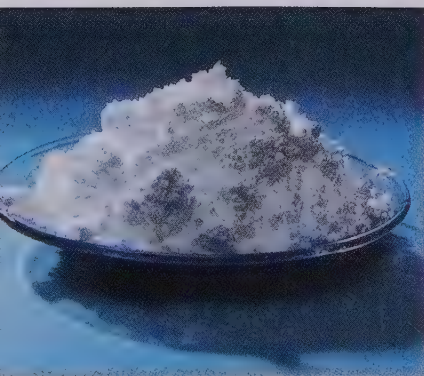
This process corresponds to the first ionization energy for lithium, which is 520 kJ/mol.

STEP 3 Dissociation of fluorine molecules. We need to form a mole of fluorine atoms by breaking the F—F bonds in a half mole of F₂ molecules:



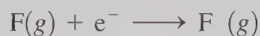
The energy required to break this bond is 154 kJ/mol. In this case we are breaking the bonds in a half mole of fluorine, so the energy required for this step is (154 kJ)/2, or 77 kJ.

The structures of ionic solids will be discussed in detail in Chapter 10.



Lithium fluoride.

STEP 4 Formation of F^- ions from fluorine atoms in the gas phase:



The energy change for this process corresponds to the electron affinity of fluorine, which is -328 kJ/mol.

STEP 5 Formation of solid lithium fluoride from the gaseous Li^+ and F^- ions:



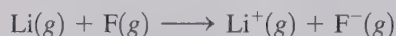
This corresponds to the lattice energy for LiF, which is -1047 kJ/mol.

Since the sum of these five processes yields the desired overall reaction, the sum of the individual energy changes gives the overall energy change:

Process	Energy Change (kJ)
$Li(s) \rightarrow Li(g)$	161
$Li(g) \rightarrow Li^+(g) + e^-$	520
$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
$F(g) + e^- \rightarrow F^-(g)$	-328
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	-1047
Overall: $Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$	-617 kJ (per mole of LiF)

In doing this calculation, we have ignored the small difference between ΔH_{sub} and ΔE_{sub} .

This process is summarized by the energy diagram in Fig. 8.8. Note that the formation of solid lithium fluoride from its elements is highly exothermic, mainly because of the very large negative lattice energy. A great deal of energy is released when the ions combine to form the solid. In fact, note that the energy released when an electron is added to a fluorine atom to form the F^- ion (328 kJ/mol) is not enough to remove an electron from lithium (520 kJ/mol). That is, when a metallic lithium atom reacts with a nonmetallic fluorine atom to form *separated* ions,



the process is endothermic and thus unfavorable. Clearly, then, the main impetus for the formation of an ionic compound rather than a covalent compound results

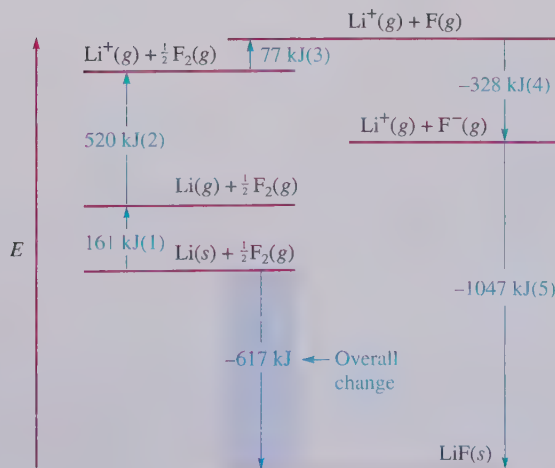
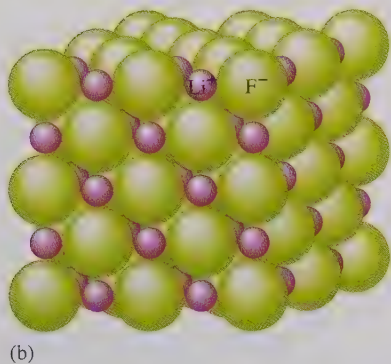
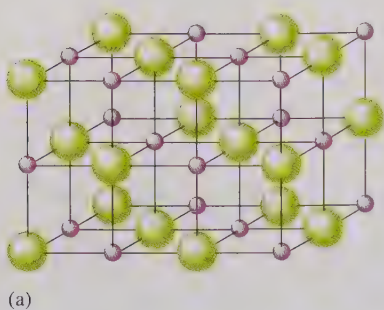


FIGURE 8.8
The energy changes involved in the formation of solid lithium fluoride from its elements. The numbers in parentheses refer to the reaction steps discussed in the text.

**FIGURE 8.9**

The structure of lithium fluoride. (a) Represented by ball-and-stick model. Note that each Li^+ ion is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions. (b) Represented with the ions shown as spheres. The structure is determined by packing the spherical ions in a way that both maximizes the ionic attractions and minimizes the ionic repulsions.

Since the equation for lattice energy contains the product Q_1Q_2 , the lattice energy for a solid with 2+ and 2- ions should be four times that for a solid with 1+ and 1- ions. That is,

$$\frac{(+2)(-2)}{(+1)(-1)} = 4$$

For MgO and NaF , the observed ratio of lattice energies (see Fig. 8.10) is

$$\frac{-3916 \text{ kJ}}{-923 \text{ kJ}} = 4.24$$

from the strong mutual attractions among the Li^+ and F^- ions in the solid. The lattice energy is the dominant energy term.

The structure of solid lithium fluoride is represented in Fig. 8.9. Note the alternating arrangement of the Li^+ and F^- ions. Also note that each Li^+ is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions. This structure can be rationalized by assuming that the ions behave as hard spheres that pack together in a way that both maximizes the attractions among the oppositely charged ions and minimizes the repulsions among the identically charged ions.

All the binary ionic compounds formed by an alkali metal and a halogen have the structure shown in Fig. 8.9, except for the cesium salts. The arrangement of ions shown in Fig. 8.9 is often called the *sodium chloride structure*, after the most common substance that possesses it.

Lattice Energy Calculations

In discussing the energetics of the formation of solid lithium fluoride, we emphasized the importance of lattice energy in contributing to the stability of the ionic solid. Lattice energy can be represented by a modified form of Coulomb's law:

$$\text{Lattice energy} = k \left(\frac{Q_1 Q_2}{r} \right)$$

where k is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions, Q_1 and Q_2 are the charges on the ions, and r is the shortest distance between the centers of the cations and anions. Note that the lattice energy has a negative sign when Q_1 and Q_2 have opposite signs. This result is expected, since bringing cations and anions together is an exothermic process. Also note that the process becomes more exothermic as the ionic charges increase and as the distances between the ions in the solid decrease.

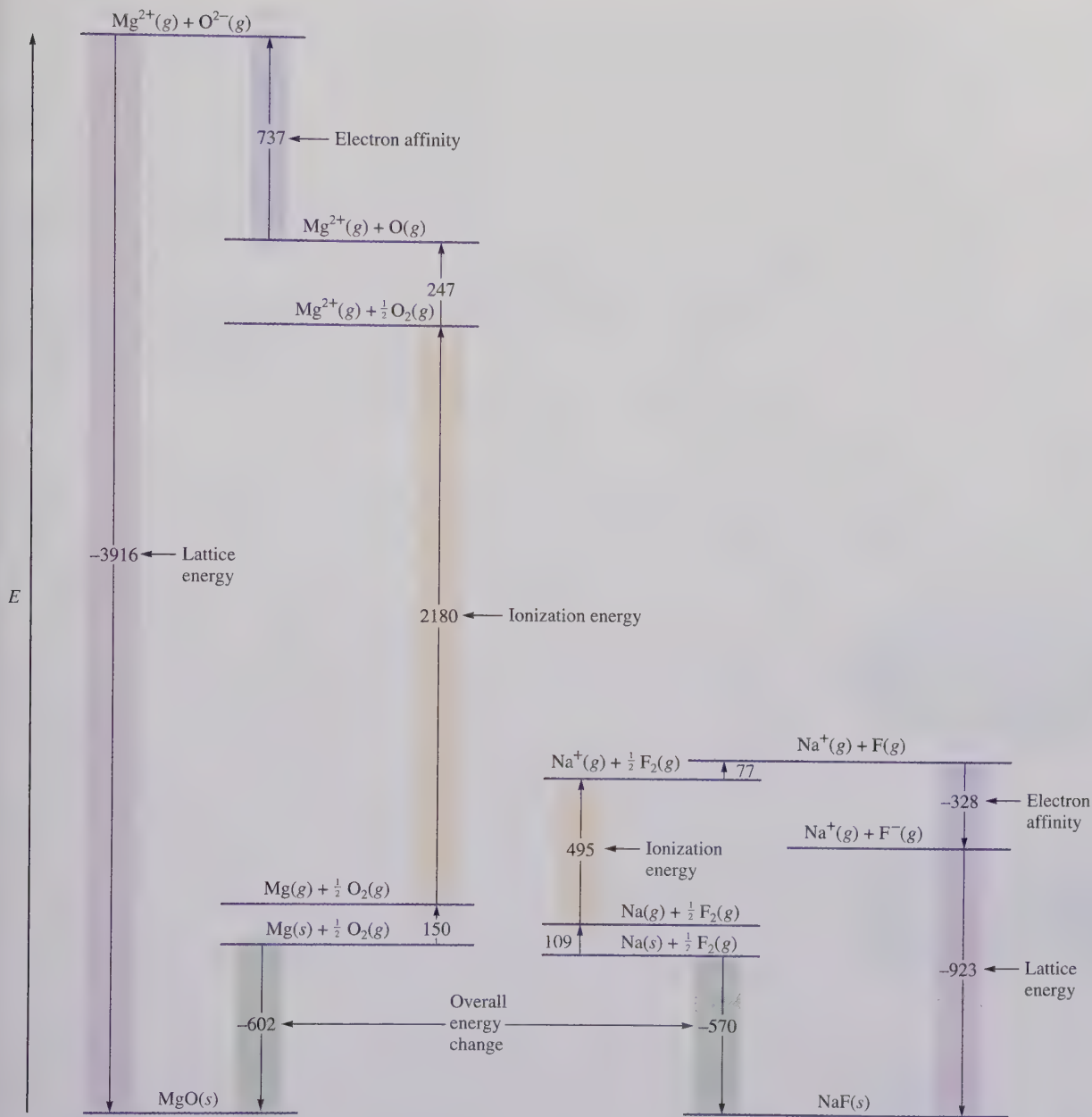
The importance of the charges in ionic solids can be illustrated by comparing the energies involved in the formation of NaF(s) and MgO(s) . These solids contain the isoelectronic ions Na^+ , F^- , Mg^{2+} , and O^{2-} . The energy diagram for the formation of the two solids is given in Fig. 8.10. Note several important features:

The energy released when the gaseous Mg^{2+} and O^{2-} ions combine to form solid MgO is much greater (more than four times greater) than that released when the gaseous Na^+ and F^- ions combine to form solid NaF .

The energy required to remove two electrons from the magnesium atom (735 kJ/mol for the first and 1445 kJ/mol for the second, yielding a total of 2180 kJ/mol) is much greater than the energy required to remove one electron from a sodium atom (495 kJ/mol).

Energy (737 kJ/mol) is required to add two electrons to the oxygen atom in the gas phase. Addition of the first electron is exothermic (−141 kJ/mol), but addition of the second electron is quite endothermic (878 kJ/mol). This latter energy must be obtained indirectly, since the $\text{O}^{2-}(\text{g})$ ion is not stable.

In view of the facts that twice as much energy is required to remove the second electron from magnesium as to remove the first and that addition of an electron to the gaseous O^- ion is quite endothermic, it seems puzzling that magnesium oxide contains Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions. The answer lies in the lattice energy. Note that the lattice energy for combining gaseous Mg^{2+}

**FIGURE 8.10**

Comparison of the energy changes involved in the formation of solid sodium fluoride and solid magnesium oxide. Note the large lattice energy for magnesium oxide (where doubly charged ions are combining) compared with that for sodium fluoride (where singly charged ions are combining).

and O^{2-} ions to form $\text{MgO}(s)$ is 3000 kJ/mol more negative than that for combining gaseous Na^+ and F^- ions to form $\text{NaF}(s)$. Thus the energy released in forming a solid containing Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions more than compensates for the energies required for the processes that produce the Mg^{2+} and O^{2-} ions.

If there is so much lattice energy to be gained in going from singly charged to doubly charged ions in the case of magnesium oxide, why then does solid sodium fluoride contain Na^+ and F^- ions rather than Na^{2+} and F^{2-} ions? We can answer this question by recognizing that both Na^+ and F^- ions have the neon electron configuration. Removal of an electron from Na^+ requires an extremely large quantity of energy (4560 kJ/mol) because a $2p$ electron must be removed. Conversely, the addition of an electron to F^- would require use of the relatively high-energy $3s$ orbital, which is also an unfavorable process. Thus we can say that for sodium fluoride the extra energy required to form the doubly charged ions is greater than the gain in lattice energy that would result.

This discussion of the energies involved in the formation of solid ionic compounds illustrates that a variety of factors operate to determine the composition and structure of these compounds. The most important of these factors involve the balancing of the energies required to form highly charged ions and the energy released when highly charged ions combine to form the solid.

8.6 Partial Ionic Character of Covalent Bonds

Recall that when atoms with different electronegativities react to form molecules, the electrons are not shared equally. The possible result is a polar covalent bond or, in the case of a large electronegativity difference, a complete transfer of one or more electrons to form ions. The cases are summarized in Fig. 8.11.

How well can we tell the difference between an ionic bond and a polar covalent bond? The only honest answer to this question is that there are probably no totally ionic bonds between *discrete pairs of atoms*. The evidence for this statement comes from calculations of the percent ionic character for the bonds of various binary compounds in the gas phase. These calculations are based on comparisons of the measured dipole moments for molecules of the type $\text{X}-\text{Y}$ with the calculated dipole moments for the completely ionic case, X^+Y^- . The percent ionic character of a bond can be defined as

$$\text{Percent ionic character of a bond} = \left(\frac{\text{measured dipole moment of } \text{X}-\text{Y}}{\text{calculated dipole moment of } \text{X}^+\text{Y}^-} \right) \times 100\%$$

Application of this definition to various compounds (in the gas phase) gives the results shown in Fig. 8.12, where percent ionic character is plotted versus the difference in the electronegativity values of X and Y . Note from this plot that ionic character increases with electronegativity difference, as expected. However, none of the bonds reaches 100% ionic character, even though compounds with the maximum possible electronegativity differences are considered. Thus, according to this definition, no individual bonds are completely ionic. This conclusion is in contrast to the usual classification of many of these compounds (as ionic solids). All the compounds shown in Fig. 8.12 with more than 50% ionic character are normally considered to be ionic solids. Recall, however, the results in Fig. 8.12 are for the gas phase, where individual XY molecules exist. These results cannot necessarily be assumed to apply to the solid state, where the existence of ions is favored by the multiple ion interactions.

Another complication in identifying ionic compounds is that many substances contain polyatomic ions. For example, NH_4Cl contains NH_4^+ and Cl^- ions, and Na_2SO_4 contains Na^+ and SO_4^{2-} ions. The ammonium and sulfate ions are held

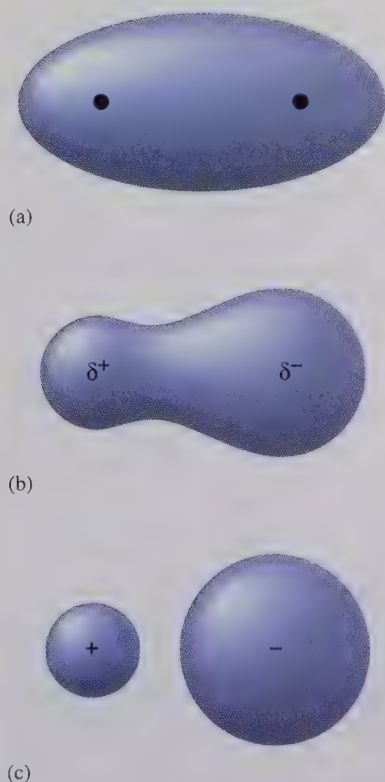
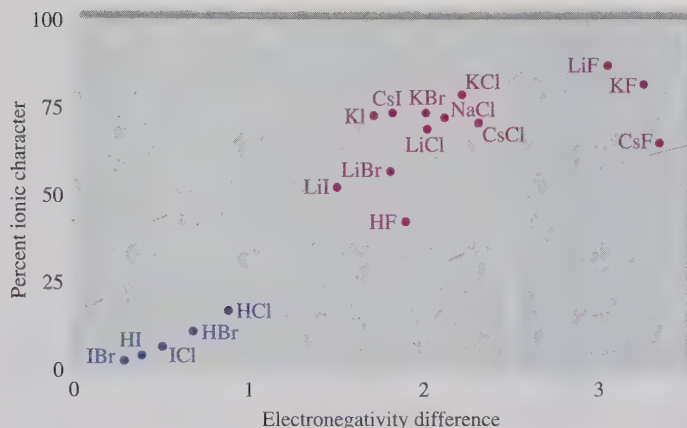


FIGURE 8.11

The three possible types of bonds: (a) a covalent bond formed between identical atoms; (b) a polar covalent bond, with both ionic and covalent components; and (c) an ionic bond with no electron sharing.

FIGURE 8.12

The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms. Note that the compounds with ionic character greater than 50% are normally considered to be ionic compounds.



together by covalent bonds. Thus, calling NH_4Cl and Na_2SO_4 ionic compounds is somewhat ambiguous.

We will avoid these problems by adopting an operational definition of ionic compounds: *Any compound that conducts an electric current when melted will be classified as ionic.*

8.7 The Covalent Chemical Bond: A Model

Before we develop specific models for covalent chemical bonding, it will be helpful to summarize some of the concepts introduced in this chapter.

What is a chemical bond? Chemical bonds can be viewed as forces that cause a group of atoms to behave as a unit.

Why do chemical bonds occur? There is no principle of nature that states that bonds are favored or disfavored. Bonds are neither inherently “good” nor inherently “bad” as far as nature is concerned; *bonds result from the tendency of a system to seek its lowest possible energy.* From a simplistic point of view, bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms. For example, approximately 1652 kJ of energy is required to break a mole of methane (CH_4) molecules into separate C and H atoms. Or, taking the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms. Thus we can say that 1 mole of CH_4 molecules in the gas phase is 1652 kJ lower in energy than 1 mole of carbon atoms plus 4 moles of hydrogen atoms. Methane is therefore a stable molecule relative to its separated atoms.

We find it useful to interpret molecular stability in terms of a model called a *chemical bond*. To understand why this model was invented, let’s continue with methane, which consists of four hydrogen atoms arranged at the corners of a tetrahedron around a carbon atom:

A tetrahedron has four equal triangular faces.



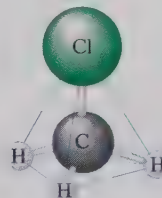


Molten NaCl conducts an electric current, indicating the presence of mobile Na^+ and Cl^- ions.

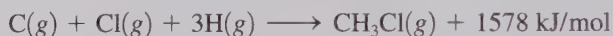
Given this structure, it is natural to envision four individual C—H interactions (we call them *bonds*). The energy of stabilization of CH_4 is divided equally among the four bonds to give an average C—H bond energy per mole of C—H bonds:

$$\frac{1652 \text{ kJ/mol}}{4} = 413 \text{ kJ/mol}$$

Next, consider methyl chloride, which consists of CH_3Cl molecules having the structure



Experiments have shown that approximately 1578 kJ of energy is required to break down 1 mole of gaseous CH_3Cl molecules into gaseous carbon, chlorine, and hydrogen atoms. The reverse process can be represented as



A mole of gaseous methyl chloride is lower in energy by 1578 kJ than its separate gaseous atoms. Thus a mole of methyl chloride is held together by 1578 kJ of energy. Again, it is very useful to divide this energy into individual bonds. Methyl chloride can be visualized as containing one C—Cl bond and three C—H bonds. If we assume arbitrarily that a C—H interaction represents the same quantity of energy in any situation (that is, that the strength of a C—H bond is independent of its molecular environment), we can do the following bookkeeping:

$$\begin{aligned} 1 \text{ mol C—Cl bonds plus } 3 \text{ mol C—H bonds} &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} + 3(\text{average C—H bond energy}) &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} + 3(413 \text{ kJ/mol}) &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} &= 1578 - 1239 = 339 \text{ kJ/mol} \end{aligned}$$

These assumptions allow us to associate given quantities of energy with C—H and C—Cl bonds.

It is important to note that the bond concept is a human invention. Bonds provide a method for dividing up the energy evolved when a stable molecule is formed from its component atoms. Thus in this context a bond represents a quantity of energy obtained from the overall molecular energy of stabilization in a rather arbitrary way. This is not to say that the concept of individual bonds is a bad idea. In fact, the modern concept of the chemical bond, conceived by the American chemists G. N. Lewis and Linus Pauling, is one of the most useful ideas chemists have ever developed.

Models: An Overview

The framework of chemistry, like that of any science, consists of *models*—attempts to explain how nature operates on the microscopic level based on experiences in the

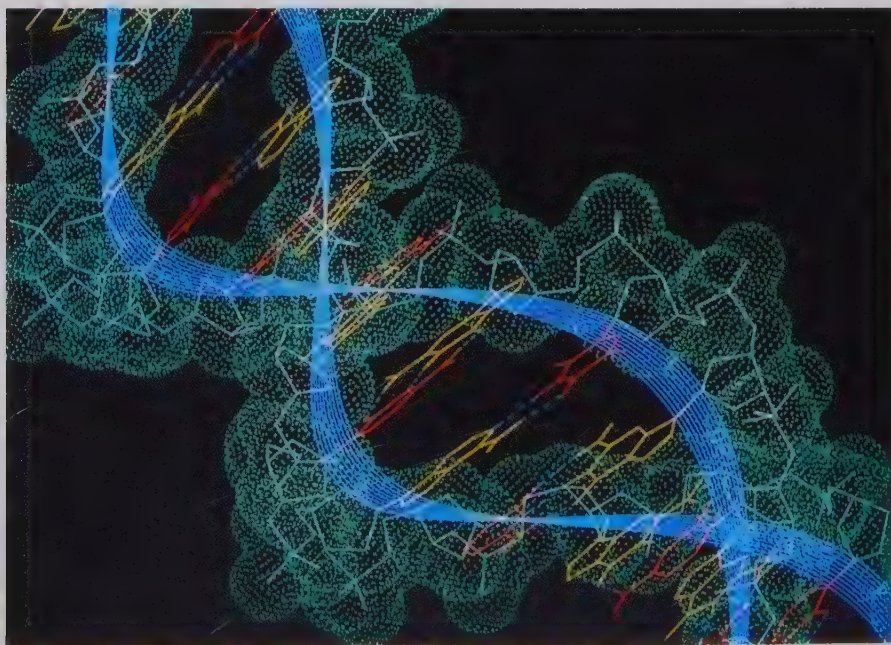
Bonding is a model proposed to explain molecular stability.

macroscopic world. To understand chemistry, one must understand its models and how they are used. We will use the concept of bonding to reemphasize the important characteristics of models, including their origin, structure, and uses.

Models originate from our observations of the properties of nature. For example, the concept of bonds arose from the observations that most chemical processes involve collections of atoms and that chemical reactions involve rearrangements of the ways the atoms are grouped. Therefore, to understand reactions, we must understand the forces that bind atoms together.

In natural processes there is a tendency toward lower energy. Collections of atoms therefore occur because the aggregated state has lower energy than the separated atoms. Why? As we saw earlier in this chapter, the best explanations for the energy change involve atoms sharing electrons or atoms transferring electrons to become ions. In the case of electron sharing, we find it convenient to assume that individual bonds occur between pairs of atoms. Let's explore the validity of this assumption and see how it is useful.

In a diatomic molecule such as H_2 , it is natural to assume that a bond exists between the atoms, holding them together. It is also useful to assume that individual bonds are present in polyatomic molecules such as CH_4 . Therefore, instead of thinking of CH_4 as a unit with a stabilization energy of 1652 kJ per mole, we choose to think of CH_4 as containing four C—H bonds, each worth 413 kJ of energy per mole of bonds. Without this concept of individual bonds in molecules, chemistry would be hopelessly complicated. There are millions of different chemical compounds, and if each of these compounds had to be considered as an entirely new entity, the task of understanding chemical behavior would be overwhelming.



The concept of individual bonds makes it much easier to deal with complex molecules such as DNA. A small segment of a DNA molecule is shown here.

The bonding model provides a framework to systematize chemical behavior by enabling us to think of molecules as collections of common fundamental components. For example, a typical biomolecule, such as a protein, contains hundreds of atoms and might seem discouragingly complex. However, if we think of a protein as constructed of individual bonds, C—C, C—H, C—N, C—O, N—H, and so on, it helps tremendously in predicting and understanding the protein's behavior. The essential idea is that we expect a given bond to behave about the same in any molecular environment. Used in this way, the model of the chemical bond has helped chemists to systematize the reactions of the millions of existing compounds.

In addition to being useful, the bonding model is physically sensible. It makes sense that atoms can form stable groups by sharing electrons; shared electrons give a lower energy state because they are simultaneously attracted by two nuclei.

Also, as we will see in the next section, bond energy data support the existence of discrete bonds that are relatively independent of the molecular environment. It is very important to remember, however, that the chemical bond is only a model. Although our concept of discrete bonds in molecules agrees with many of our observations, some molecular properties require that we think of a molecule as a whole, with the electrons free to move through the entire molecule. This is called *delocalization* of the electrons, a concept that will be discussed more completely in the next chapter.

Fundamental Properties of Models

- Models are human inventions, always based on an incomplete understanding of how nature works. *A model does not equal reality.*
- Models are often wrong. This property derives from the first property. Models are based on speculation and are always oversimplifications.
- Models tend to become more complicated as they age. As flaws are discovered in our models, we “patch” them and thus add more detail.
- It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can be expected to yield only qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.

For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple aufbau principle used to account for the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper, for example, do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the simple model. However, this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we must apply it with caution and not expect it to be correct in every case.

- When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes. (Try to remember this when you get back your next chemistry test.)

8.8 Covalent Bond Energies and Chemical Reactions

In this section we will consider the energies associated with various types of bonds and see how the bonding concept is useful in dealing with the energies of chemical reactions. One important consideration is to establish the sensitivity of a particular type of bond to its molecular environment. For example, consider the stepwise decomposition of methane:

Process	Energy Required (kJ/mol)
$\text{CH}_4(g) \rightarrow \text{CH}_3(g) + \text{H}(g)$	435
$\text{CH}_3(g) \rightarrow \text{CH}_2(g) + \text{H}(g)$	453
$\text{CH}_2(g) \rightarrow \text{CH}(g) + \text{H}(g)$	425
$\text{CH}(g) \rightarrow \text{C}(g) + \text{H}(g)$	339
	Total = 1652
	Average = $\frac{1652}{4} = 413$

Although a C—H bond is broken in each case, the energy required varies in a nonsystematic way. This example shows that the C—H bond is somewhat sensitive to its environment. We use the *average* of these individual bond dissociation energies even though this quantity only approximates the energy associated with a C—H bond in a particular molecule. The degree of sensitivity of a bond to its environment also can be seen from experimental measurements of the energy required to break the C—H bond in the following molecules:

Molecule	Measured C—H Bond Energy (kJ/mol)
HCBBr_3	380
HCCl_3	380
HCF_3	430
C_2H_6	410

These data show that the C—H bond strength varies significantly with its environment, but the concept of an average C—H bond strength remains useful to chemists. The average values of bond energies for various types of bonds are listed in Table 8.4.

So far we have discussed bonds in which one pair of electrons is shared. This type of bond is called a **single bond**. As we will see in more detail later, atoms sometimes share two pairs of electrons, forming a **double bond**, or share three pairs of electrons, forming a **triple bond**. The bond energies for these *multiple bonds* are also given in Table 8.4.

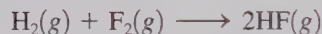
A relationship also exists between the number of shared electron pairs and the bond length. As the number of shared electrons increases, the bond length shortens. This relationship is shown for selected bonds in Table 8.5.

Bond Energy and Enthalpy

Bond energy values can be used to calculate approximate energies for reactions. To illustrate how this is done, we will calculate the change in energy that accompanies the following reaction:

TABLE 8.4 Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO₂) = 799

This reaction involves breaking one H—H and one F—F bond and forming two H—F bonds. For bonds to be broken, energy must be *added* to the system—an endothermic process. Consequently, the energy terms associated with bond breaking have *positive* signs. The formation of a bond *releases* energy, an exothermic process, so the energy terms associated with bond making carry a *negative* sign. We can write the enthalpy change for a reaction as follows:

$$\Delta H = \text{sum of the energies required to break old bonds (positive signs)} \\ \text{plus the sum of the energies released in the formation of new} \\ \text{bonds (negative signs)}$$

TABLE 8.5 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C=O	Double	123	745
C—N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

This leads to the expression

$$\Delta H = \underbrace{\sum D \text{ (bonds broken)}}_{\text{Energy required}} - \underbrace{\sum D \text{ (bonds formed)}}_{\text{Energy released}}$$

where Σ represents the sum of terms, and D represents the bond energy per mole of bonds. (D always has a positive sign.)

In the case of the formation of HF,

$$\begin{aligned}\Delta H &= D_{\text{H-H}} + D_{\text{F-F}} - 2D_{\text{H-F}} \\ &= 1 \text{ mol} \times \frac{432 \text{ kJ}}{\text{mol}} + 1 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} - 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} \\ &= -544 \text{ kJ}\end{aligned}$$

Thus, when 1 mol $\text{H}_2(\text{g})$ and 1 mol $\text{F}_2(\text{g})$ react to form 2 mol $\text{HF}(\text{g})$, 544 kJ of energy should be released.

This result can be compared with the calculation of ΔH for this reaction from the standard enthalpy of formation for HF (-271 kJ/mol):

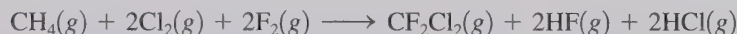
$$\Delta H^\circ = 2 \text{ mol} \times (-271 \text{ kJ/mol}) = -542 \text{ kJ}$$

Thus the use of bond energies to calculate ΔH works quite well in this case.

SAMPLE EXERCISE 8.5

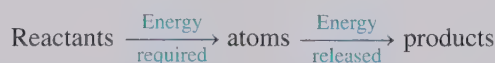
ΔH from Bond Energies

Using the bond energies listed in Table 8.4, calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2).



SOLUTION

The idea here is to break the bonds in the gaseous reactants to give individual atoms and then assemble these atoms into the gaseous products by forming new bonds:



We then combine the energy changes to calculate ΔH :

$$\Delta H = \text{energy required to break bonds} - \text{energy released when bonds form}$$

where the minus sign gives the correct sign to the energy terms for the exothermic processes.

Reactant Bonds Broken:

CH_4 : 4 mol C—H	$4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$
2Cl_2 : 2 mol Cl—Cl	$2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$
2F_2 : 2 mol F—F	$2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = 308 \text{ kJ}$
	Total energy required = 2438 kJ

Product Bonds Formed:

$$\begin{array}{llll}
 \text{CF}_2\text{Cl}_2: & 2 \text{ mol C—F} & 2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = & 970 \text{ kJ} \\
 & \text{and} & & \\
 & 2 \text{ mol C—Cl} & 2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = & 678 \text{ kJ} \\
 \text{HF:} & 2 \text{ mol H—F} & 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = & 1130 \text{ kJ} \\
 \text{HCl:} & 2 \text{ mol H—Cl} & 2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = & 854 \text{ kJ} \\
 & & \text{Total energy released} = & 3632 \text{ kJ}
 \end{array}$$

We now can calculate ΔH :

$$\begin{aligned}
 \Delta H &= \text{energy required to break bonds} - \text{energy released when bonds form} \\
 &= 2438 \text{ kJ} - 3632 \text{ kJ} \\
 &= -1194 \text{ kJ}
 \end{aligned}$$

Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of CF_2Cl_2 formed.

See Exercises 8.47 through 8.52.

8.9 The Localized Electron Bonding Model

So far we have discussed the general characteristics of the chemical bonding model and have seen that properties such as bond strength and polarity can be assigned to individual bonds. In this section we introduce a specific model used to describe covalent bonds. We need a simple model that can be applied easily even to very complicated molecules and that can be used routinely by chemists to interpret and organize the wide variety of chemical phenomena. The model that serves this purpose is the **localized electron (LE) model**, which assumes that *a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms*. Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called **lone pairs**, and those found in the space between the atoms are called **bonding pairs**.

As we will apply it, the LE model has three parts:

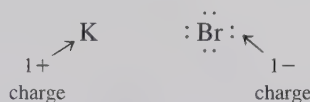
1. Description of the valence electron arrangement in the molecule using Lewis structures (will be discussed in the next section).
2. Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model (will be discussed in Section 8.13).
3. Description of the type of atomic orbitals used by the atoms to share electrons or hold lone pairs (will be discussed in Chapter 9).

8.10 Lewis Structures

Lewis structures show only valence electrons.

The **Lewis structure** of a molecule shows how the valence electrons are arranged among the atoms in the molecule. These representations are named after G. N. Lewis (Fig. 8.13). The rules for writing Lewis structures are based on observations of thousands of molecules. From experiment, chemists have learned that the *most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configurations*.

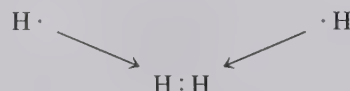
We have already seen that when metals and nonmetals react to form binary ionic compounds, electrons are transferred and the resulting ions typically have noble gas electron configurations. An example is the formation of KBr, where the K^+ ion has the [Ar] electron configuration and the Br^- ion has the [Kr] electron configuration. In writing Lewis structures, the rule is that *only the valence electrons are included*. Using dots to represent electrons, the Lewis structure for KBr is



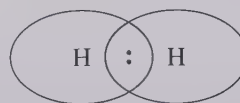
No dots are shown on the K^+ ion because it has no valence electrons. The Br^- ion is shown with eight electrons because it has a filled valence shell.

Next we will consider Lewis structures for molecules with covalent bonds, involving elements in the first and second periods. The principle of achieving a noble gas electron configuration applies to these elements as follows:

- Hydrogen forms stable molecules where it shares two electrons. That is, it follows a **duet rule**. For example, when two hydrogen atoms, each with one electron, combine to form the H_2 molecule, we have



By sharing electrons, each hydrogen in H_2 , in effect, has two electrons; that is, each hydrogen has a filled valence shell.



- Helium does not form bonds because its valence orbital is already filled; it is a noble gas. Helium has the electron configuration $1s^2$ and can be represented by the Lewis structure



- The second-row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the $2s$ and the three $2p$ orbitals. Since eight electrons are required to fill these

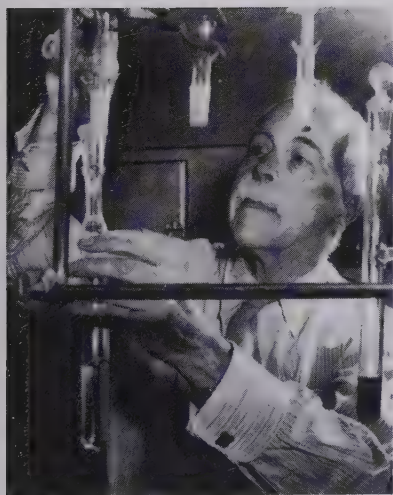


FIGURE 8.13
G. N. Lewis (1875–1946).

Carbon, nitrogen, oxygen, and fluorine always obey the octet rule in stable molecules.

orbitals, these elements typically obey the **octet rule**; they are surrounded by eight electrons. An example is the F_2 molecule, which has the following Lewis structure:



Note that each fluorine atom in F_2 is, in effect, surrounded by eight electrons, two of which are shared with the other atom. This is a *bonding pair* of electrons, as discussed earlier. Each fluorine atom also has three pairs of electrons not involved in bonding. These are the *lone pairs*.

- Neon does not form bonds because it already has an octet of valence electrons (it is a noble gas). The Lewis structure is



Note that only the valence electrons of the neon atom ($2s^2 2p^6$) are represented by the Lewis structure. The $1s^2$ electrons are core electrons and are not shown.

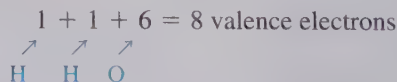
From the preceding discussion we can formulate the following rules for writing the Lewis structures of molecules containing atoms from the first two periods.

Steps for Writing Lewis Structures

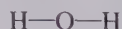
- ➡ **1** Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
- ➡ **2** Use a pair of electrons to form a bond between each pair of bound atoms.
- ➡ **3** Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

To see how these steps are applied, we will draw the Lewis structures of a few molecules. We will first consider the water molecule and follow the previous steps.

- ➡ **1** We sum the *valence* electrons for H_2O as shown:



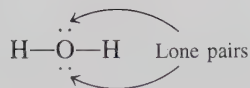
- ➡ **2** Using a pair of electrons per bond, we draw in the two O—H single bonds:



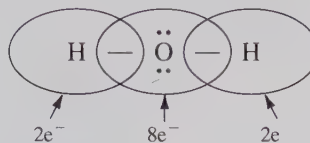
Note that a *line instead of a pair of dots is used to indicate each pair of bonding electrons*. This is the standard notation.

- ➡ **3** We distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons have been used in forming the two bonds, four electrons ($8 - 4$) remain to be distributed. Hydrogen is satisfied with two electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration. Thus the remaining four electrons are added to oxygen as two lone pairs. Dots are used to represent the lone pairs:

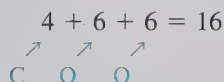
$\text{H}-\text{O}-\text{H}$ represents $\text{H}:\text{O}:\text{H}$



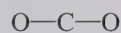
This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight, as shown below:



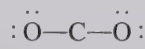
As a second example, let's write the Lewis structure for carbon dioxide. Summing the valence electrons gives



After forming a bond between the carbon and each oxygen,



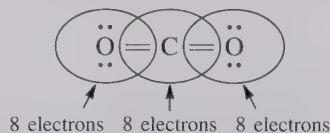
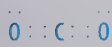
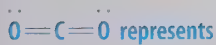
the remaining electrons are distributed to achieve noble gas configurations on each atom. In this case we have 12 electrons ($16 - 4$) remaining after the bonds are drawn. The distribution of these electrons is determined by a trial-and-error process. We have 6 pairs of electrons to distribute. Suppose we try 3 pairs on each oxygen to give



Is this correct? To answer this question, we need to check two things:

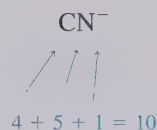
1. The total number of electrons. There are 16 valence electrons in this structure, which is the correct number.
2. The octet rule for each atom. Each oxygen has 8 electrons, but the carbon has only 4. This cannot be the correct Lewis structure.

How can we arrange the 16 available electrons to achieve an octet for each atom? Suppose there are 2 shared pairs between the carbon and each oxygen:



Now each atom is surrounded by 8 electrons, and the total number of electrons is 16, as required. This is the correct Lewis structure for carbon dioxide, which has two double bonds and four lone pairs.

Finally, let's consider the Lewis structure of the CN^- (cyanide) ion. Summing the valence electrons, we have



Note that the negative charge means an extra electron is present. After drawing a single bond ($\text{C}-\text{N}$), we distribute the remaining electrons to achieve a noble gas

configuration for each atom. Eight electrons remain to be distributed. We can try various possibilities, for example:



This structure is incorrect because C and N have only six electrons each instead of eight. The correct arrangement is



(Satisfy yourself that both carbon and nitrogen have eight electrons.)

SAMPLE EXERCISE 8.6

Writing Lewis Structures

Give the Lewis structure for each of the following.

- a. HF d. CH₄
b. N₂ e. CF₄
c. NH₃ f. NO⁺

SOLUTION

In each case we apply the three steps for writing Lewis structures. Recall that lines are used to indicate shared electron pairs and that dots are used to indicate non-bonding pairs (lone pairs). We have the following tabulated results:

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	1 + 7 = 8	H—F	6	H— $\ddot{\text{F}}:$	H, 2 F, 8
b. N ₂	5 + 5 = 10	N—N	8	:N≡N:	N, 8
c. NH ₃	5 + 3(1) = 8	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	2	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 N, 8
d. CH ₄	4 + 4(1) = 8	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	0	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 C, 8
e. CF ₄	4 + 4(7) = 32	$\begin{array}{c} \text{F} \\ \\ \text{F} - \text{C} - \text{F} \\ \\ \text{F} \end{array}$	24	$\begin{array}{c} :\ddot{\text{F}}: \\ \\ :\ddot{\text{F}}: - \text{C} - :\ddot{\text{F}}: \\ \\ :\ddot{\text{F}}: \end{array}$	F, 8 C, 8
f. NO ⁺	5 + 6 - 1 = 10	N—O	8	[:N≡O:] ⁺	N, 8 O, 8

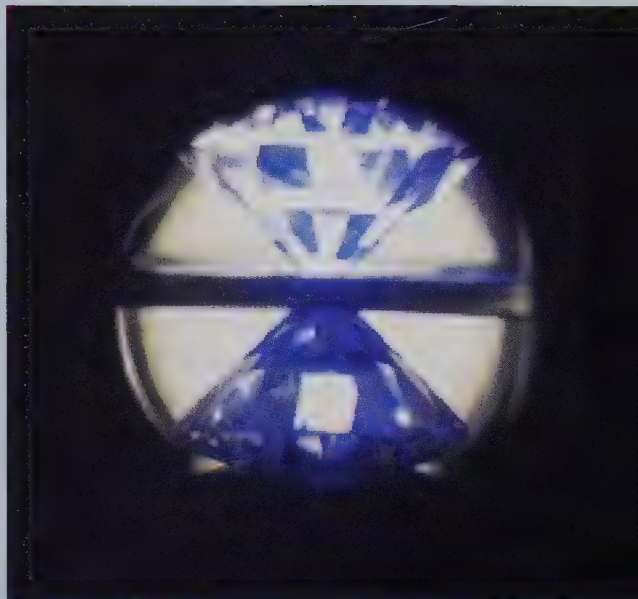
See Exercises 8.61 and 8.62.

CHEMICAL IMPACT

Nitrogen Under Pressure

The element nitrogen exists at normal temperatures and pressures as a gas containing N_2 , a molecule with a very strong triple bond. In the gas phase the diatomic molecules move around independently with almost no tendency to associate with each other. Under intense pressure, however, nitrogen changes to a dramatically different form. This conclusion was reached at the Carnegie Institution in Washington, D.C., by Mikhail Erements and his colleagues, who subjected nitrogen to a pressure of 2.4 million atmospheres in a special diamond anvil press. Under this tremendous pressure the bonds of the N_2 molecules break and a substance containing an aggregate of nitrogen atoms forms. In other words, under great pressure elemental nitrogen changes from a substance containing diatomic molecules to one containing many nitrogen atoms bonded to each other. Interestingly, this substance remains intact even after the pressure is released—as long as the temperature remains at 100 K. This new form of nitrogen has a very high potential energy relative to N_2 . Thus this substance would be an extraordinarily powerful propellant or explosive if enough of it could be made. This new form of nitrogen is also a semiconductor for electricity; normal nitrogen gas is an insulator.

The newly discovered form of nitrogen is significant for several reasons. For one thing, it may help us understand the nature of the interiors of the giant gas planets such as Jupiter. Also, their success in changing nitrogen to an atomic solid encourages high-pressure scientists who are trying to accomplish the same goal with hydrogen. It is surprising that



A diamond anvil cell used to study materials at very high pressures.

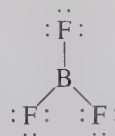
nitrogen, which has diatomic molecules containing bonds more than twice as strong as those in hydrogen, will form an atomic solid at these pressures but hydrogen does not. Hydrogen remains a molecular solid at far greater pressures than nitrogen can endure.

When writing Lewis structures, do not worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all the available valence electrons of the atoms to achieve the lowest possible energy.* The valence electrons belong to the molecule, rather than to the individual atoms. Simply distribute all valence electrons so that the various rules are satisfied, without regard for the origin of each particular electron.

*In a sense this approach corrects for the fact that the localized electron model overemphasizes that a molecule is simply a sum of its parts—that is, that the atoms retain their individual identities in the molecule.

8.11 Exceptions to the Octet Rule

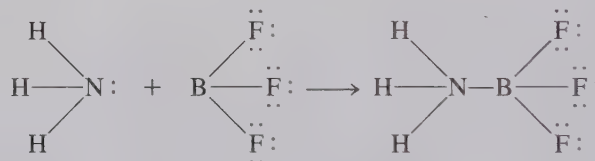
The localized electron model is a simple but very successful model, and the rules we have used for Lewis structures apply to most molecules. However, with such a simple model, some exceptions are inevitable. Boron, for example, tends to form compounds in which the boron atom has fewer than eight electrons around it—it does not have a complete octet. Boron trifluoride (BF_3), a gas at normal temperatures and pressures, reacts very energetically with molecules such as water and ammonia that have available electron pairs (lone pairs). The violent reactivity of BF_3 with electron-rich molecules arises because the boron atom is electron-deficient. Boron trifluoride has 24 valence electrons. The Lewis structure often drawn for BF_3 is



Note that in this structure boron has only 6 electrons around it. The octet rule for boron can be satisfied by drawing a structure with a double bond, such as



Recent studies indicate that double bonding may be important in BF_3 . However, the boron atom in BF_3 certainly behaves as if it is electron-deficient, as indicated by the reactivity of BF_3 toward electron-rich molecules, for example, toward NH_3 to form H_3NBF_3 :



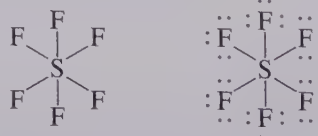
In this stable compound, boron has an octet of electrons.

It is characteristic of boron to form molecules in which the boron atom is electron-deficient. On the other hand, carbon, nitrogen, oxygen, and fluorine can be counted on to obey the octet rule.

Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond. To see how this arises, we will consider the Lewis structure for sulfur hexafluoride (SF_6), a well-known and very stable molecule. The sum of the valence electrons is

$$6 + 6(7) = 48 \text{ electrons}$$

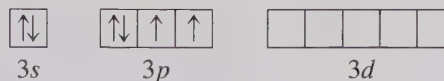
Indicating the single bonds gives the structure on the left below:



We have used 12 electrons to form the S—F bonds, which leaves 36 electrons. Since fluorine always follows the octet rule, we complete the six fluorine octets to give the structure on the right above. This structure uses all 48 valence electrons for SF_6 ,

but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule. How can this happen?

To answer this question, we need to consider the different types of valence orbitals characteristic of second- and third-period elements. The second-row elements have $2s$ and $2p$ valence orbitals, and the third-row elements have $3s$, $3p$, and $3d$ orbitals. The $3s$ and $3p$ orbitals fill with electrons in going from sodium to argon, but the $3d$ orbitals remain empty. For example, the valence orbital diagram for a sulfur atom is



Third-row elements can exceed the octet rule.

The localized electron model assumes that the empty $3d$ orbitals can be used to accommodate extra electrons. Thus the sulfur atom in SF_6 can have 12 electrons around it by using the $3s$ and $3p$ orbitals to hold 8 electrons, with the extra 4 electrons placed in the formerly empty $3d$ orbitals.

Lewis Structures: Comments About the Octet Rule

- The second-row elements C, N, O, and F should always be assumed to obey the octet rule.
- The second-row elements B and Be often have fewer than eight electrons around them in their compounds. These electron-deficient compounds are very reactive.
- The second-row elements never exceed the octet rule, since their valence orbitals ($2s$ and $2p$) can accommodate only eight electrons.
- Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty valence d orbitals.
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available d orbitals (elements in Period 3 or beyond).

Whether the atoms that exceed the octet rule actually place the extra electrons in their d orbitals is a matter of controversy among theoretical chemists. We will not consider this issue in this text.

SAMPLE EXERCISE 8.7

Lewis Structures for Molecules That Violate the Octet Rule I

Write the Lewis structure for PCl_5 .

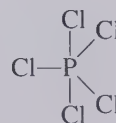
SOLUTION

We can follow the same stepwise procedure we used above for sulfur hexafluoride.

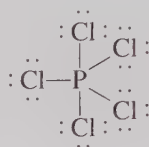
➡ **1** Sum the valence electrons.

$$\begin{array}{c} 5 + 5(7) = 40 \text{ electrons} \\ \uparrow \qquad \uparrow \\ \text{P} \qquad \text{Cl} \end{array}$$

➡ **2** Indicate single bonds between bound atoms.



➡ **3** Distribute the remaining electrons. In this case, 30 electrons ($40 - 10$) remain. These are used to satisfy the octet rule for each chlorine atom. The final Lewis structure is



Note that phosphorus, which is a third-row element, has exceeded the octet rule by two electrons.

See Exercises 8.63 and 8.64.

In the PCl_5 and SF_6 molecules, the central atoms (P and S, respectively) must have the extra electrons. However, in molecules having more than one atom that can exceed the octet rule, it is not always clear which atom should have the extra electrons. Consider the Lewis structure for the triiodide ion (I_3^-), which has

$$\begin{array}{c} 3(7) + 1 = 22 \text{ valence electrons} \\ \uparrow \quad \uparrow \\ 1 \quad 1 - \text{charge} \end{array}$$

Indicating the single bonds gives I—I—I . At this point, 18 electrons ($22 - 4$) remain. Trial and error will convince you that one of the iodine atoms must exceed the octet rule, but *which* one?

The rule we will follow is that *when it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom*.

Thus for I_3^- the Lewis structure is



where the central iodine exceeds the octet rule. This structure agrees with known properties of I_3^- .

SAMPLE EXERCISE 8.8

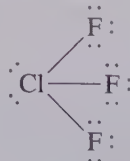
Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structure for each molecule or ion.

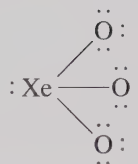
- a. ClF_3 b. XeO_3 c. RnCl_2 d. BeCl_2 e. ICl_4^-

SOLUTION

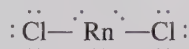
- a. The chlorine atom (third row) accepts the extra electrons.



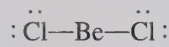
b. All atoms obey the octet rule.



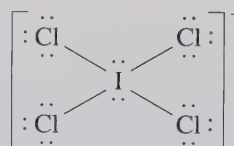
c. Radon, a noble gas in Period 6, accepts the extra electrons.



d. Beryllium is electron-deficient.



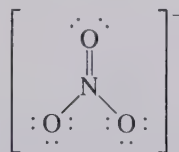
e. Iodine exceeds the octet rule.



See Exercises 8.63 and 8.64.

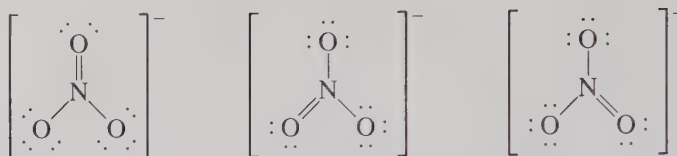
8.12 Resonance

Sometimes more than one valid Lewis structure (one that obeys the rules we have outlined) is possible for a given molecule. Consider the Lewis structure for the nitrate ion (NO_3^-), which has 24 valence electrons. To achieve an octet of electrons around each atom, a structure like this is required:



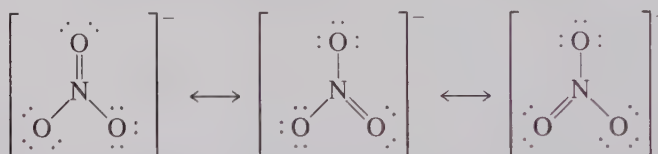
If this structure accurately represents the bonding in NO_3^- , there should be two types of N---O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds). However, experiments clearly show that NO_3^- exhibits only *one* type of N---O bond with a length and strength *between* those expected for a single bond and a double bond. Thus, although the structure we have shown above is a valid Lewis structure, it does *not* correctly represent the bonding in NO_3^- . This is a serious problem, and it means that the model must be modified.

Look again at the proposed Lewis structure for NO_3^- . There is no reason for choosing a particular oxygen atom to have the double bond. There are really three valid Lewis structures:



Is any of these structures a correct description of the bonding in NO_3^- ? No, because NO_3^- does not have one double and two single bonds—it has three equivalent bonds. We can solve this problem by making the following assumption: The correct description of NO_3^- is *not given by any one* of the three Lewis structures but is given only by the *superposition of all three*.

The nitrate ion does not exist as any of the three extreme structures but exists as an average of all three. **Resonance** is invoked when more than one valid Lewis structure can be written for a particular molecule. The resulting electron structure of the molecule is given by the average of these **resonance structures**. This situation is usually represented by double-headed arrows as follows:



Note that in all these resonance structures the arrangement of the nuclei is the same. Only the placement of the electrons differs. The arrows do not mean that the molecule “flips” from one resonance to another. They simply show that the *actual structure is an average of the three resonance structures*.

The concept of resonance is necessary because the localized electron model postulates that electrons are localized between a given pair of atoms. However, nature does not really operate this way. Electrons are really delocalized—they can move around the entire molecule. The valence electrons in the NO_3^- molecule distribute themselves to provide equivalent $\text{N}=\text{O}$ bonds. Resonance is necessary to compensate for the defective assumption of the localized electron model. However, this model is so useful that we retain the concept of localized electrons and add resonance to allow the model to treat species such as NO_3^- .

SAMPLE EXERCISE 8.9

Resonance Structures

Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model.

SOLUTION

We will follow the usual procedure for obtaining the Lewis structure for the NO_2^- ion. In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons. Indicating the single bonds gives the structure



The remaining 14 electrons ($18 - 4$) can be distributed to produce these structures:



This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two.* There are two equivalent N---O bonds, each one intermediate between a single and a double bond.

See Exercises 8.65 through 8.70.

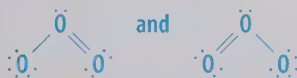
Odd-Electron Molecules

Relatively few molecules formed from nonmetals contain odd numbers of electrons. One common example is nitric oxide (NO), which is formed when nitrogen and oxygen gases react at the high temperatures in automobile engines. Nitric oxide is emitted into the air, where it immediately reacts with oxygen to form gaseous nitrogen dioxide (NO₂), another odd-electron molecule.

Since the localized electron model is based on pairs of electrons, it does not handle odd-electron cases in a natural way. To treat odd-electron molecules, a more sophisticated model is needed.

Formal Charge

Equivalent Lewis structures contain the same numbers of single and multiple bonds. For example, the resonance structures for O₃



are equivalent Lewis structures. These are equally important in describing the bonding in O₃. Nonequivalent Lewis structures contain different numbers of single and multiple bonds.

Molecules or polyatomic ions containing atoms that can exceed the octet rule often have many nonequivalent Lewis structures, all of which obey the rules for writing Lewis structures. For example, as we will see in detail below, the sulfate ion has a Lewis structure with all single bonds and several Lewis structures that contain double bonds. How do we decide which of the many possible Lewis structures best describes the actual bonding in sulfate? One method is to estimate the charge on each atom in the various possible Lewis structures and use these charges to select the most appropriate structure(s). We will see below how this is done, but first we must decide on a method to assign atomic charges in molecules.

In Chapter 4 we discussed one system for obtaining charges, called *oxidation states*. However, in assigning oxidation states, we always count *both* the shared electrons as belonging to the more electronegative atom in a bond. This practice leads to highly exaggerated estimates of charge. In other words, although oxidation states are useful for bookkeeping electrons in redox reactions, they are not realistic estimates of the actual charges on individual atoms in a molecule, so they are not suitable for judging the appropriateness of Lewis structures. Another definition of the charge on an atom in a molecule, the **formal charge**, can, however, be used to evaluate Lewis structures. As we will see below, the **formal charge** of an atom in a molecule is *the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule*.

Therefore, to determine the formal charge of a given atom in a molecule, we need to know two things:

1. The number of valence electrons on the free neutral atom (which has zero net charge because the number of electrons equals the number of protons)
2. The number of valence electrons “belonging” to the atom in a molecule

We then compare these numbers. If in the molecule the atom has the same number of valence electrons as it does in the free state, the positive and negative charges just balance, and it has a formal charge of zero. If the atom has one more valence electron in a molecule than it has as a free atom, it has a formal charge of -1 , and so on. Thus the formal charge on an atom in a molecule is defined as

$$\begin{aligned} \text{Formal charge} &= (\text{number of valence electrons on free atom}) \\ &\quad - (\text{number of valence electrons assigned to the atom in the molecule}) \end{aligned}$$

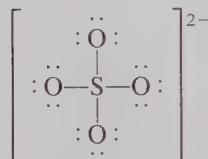
To compute the formal charge of an atom in a molecule, we assign the valence electrons in the molecule to the various atoms, making the following assumptions:

1. Lone pair electrons belong entirely to the atom in question.
2. Shared electrons are *divided equally* between the two sharing atoms.

Thus the number of valence electrons assigned to a given atom is calculated as follows:

$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2} (\text{number of shared electrons})$$

We will illustrate the procedure for calculating formal charges by considering two of the possible Lewis structures for the sulfate ion, which has 32 valence electrons. For the Lewis structure



each oxygen atom has 6 lone pair electrons and shares 2 electrons with the sulfur atom. Thus, using the preceding assumptions, each oxygen is assigned 7 valence electrons.

$$\text{Valence electrons assigned to each oxygen} = 6 \text{ plus } \frac{1}{2}(2) = 7$$

$\uparrow \qquad \uparrow$
 Lone Shared
 pair electrons
 electrons

$$\text{Formal charge on oxygen} = 6 \text{ minus } 7 = -1$$

$\uparrow \qquad \uparrow$
 Valence electrons Valence electrons
 on a free O atom assigned to each O
 in SO_4^{2-}

The formal charge on each oxygen is -1 .

For the sulfur atom there are no lone pair electrons, and eight electrons are shared with the oxygen atoms. Thus, for sulfur,

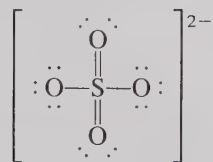
$$\text{Valence electrons assigned to sulfur} = 0 \text{ plus } \frac{1}{2}(8) = 4$$

$\uparrow \qquad \uparrow$
 Lone Shared
 pair electrons
 electrons

$$\text{Formal charge on sulfur} = 6 \text{ minus } 4 = 2$$

$\uparrow \qquad \uparrow$
 Valence electrons Valence electrons
 on a free S atom assigned to S
 in SO_4^{2-}

A second possible Lewis structure is



In this case the formal charges are as follows:

For oxygen atoms with single bonds:

$$\text{Valence electrons assigned} = 6 + \frac{1}{2}(2) = 7$$

$$\text{Formal charge} = 6 - 7 = -1$$

For oxygen atoms with double bonds:

$$\text{Valence electrons assigned} = 4 + \frac{1}{2}(4) = 6$$

↑
Each double
bond has 4
electrons

$$\text{Formal charge} = 6 - 6 = 0$$

For the sulfur atom:

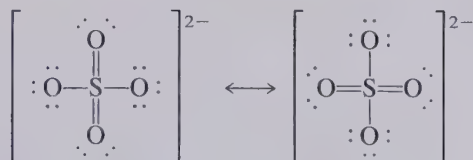
$$\text{Valence electrons assigned} = 0 + \frac{1}{2}(12) = 6$$

$$\text{Formal charge} = 6 - 6 = 0$$

We will use two fundamental assumptions about formal charges to evaluate Lewis structures:

1. Atoms in molecules try to achieve formal charges as close to zero as possible.
2. Any negative formal charges are expected to reside on the most electronegative atoms.

We can use these principles to evaluate the two Lewis structures for sulfate given previously. Notice that in the structure with only single bonds, each oxygen has a formal charge of -1 , while the sulfur has a formal charge of $+2$. In contrast, in the structure with two double bonds and two single bonds, the sulfur and two oxygen atoms have a formal charge of 0, while two oxygens have a formal charge of -1 . Based on the assumptions given above, the structure with two double bonds is preferred—it has lower formal charges and the -1 formal charges are on electronegative oxygen atoms. Thus, for the sulfate ion, we might expect resonance structures such as



to more closely describe the bonding than the Lewis structure with only single bonds.

Rules Governing Formal Charge

■ To calculate the formal charge on an atom:

1. Take the sum of the lone pair electrons and one-half the shared electrons. This is the number of valence electrons assigned to the atom in the molecule.
2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge.

■ The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.

■ If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion.

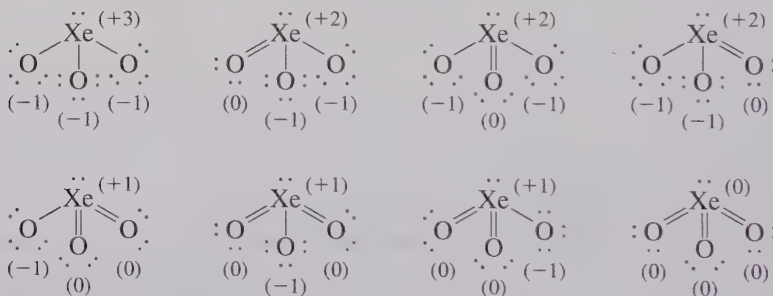
SAMPLE EXERCISE 8.10

Formal Charges

Give possible Lewis structures for XeO_3 , an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

SOLUTION

For XeO_3 (26 valence electrons) we can draw the following possible Lewis structures (formal charges are indicated in parentheses):



Based on the ideas of formal charge, we would predict that the Lewis structures with the lower values of formal charge would be most appropriate for describing the bonding in XeO_3 .

See Exercises 8.73 through 8.76.

As a final note, there are a couple of cautions about formal charge to keep in mind. First, although formal charges are closer to actual atomic charges in molecules than are oxidation states, formal charges still provide only *estimates* of charge—they should not be taken as actual atomic charges. Second, the evaluation of Lewis structures using formal charge ideas can lead to erroneous predictions. Tests based on experiments must be used to make the final decisions on the correct description of the bonding in a molecule or polyatomic ion.

8.13 Molecular Structure: The VSEPR Model

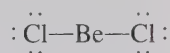


Understanding Concepts: The VSEPR Theory of Molecular Structure

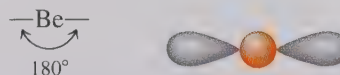
BeCl_2 has only four electrons around Be and is expected to be very reactive with electron-pair donors.

The structures of molecules play a very important role in determining their chemical properties. As we will see later, this is particularly important for biological molecules; a slight change in the structure of a large biomolecule can completely destroy its usefulness to a cell or may even change the cell from a normal one to a cancerous one.

Many accurate methods now exist for determining **molecular structure**, the three-dimensional arrangement of the atoms in a molecule. These methods must be used if precise information about structure is required. However, it is often useful to be able to predict the approximate molecular structure of a molecule. In this section we consider a simple model that allows us to do this. This model, called the **valence shell electron-pair repulsion (VSEPR) model**, is useful in predicting the geometries of molecules formed from nonmetals. The main postulate of this model is that *the structure around a given atom is determined principally by minimizing electron-pair repulsions*. The idea here is that the bonding and nonbonding pairs around a given atom will be positioned as far apart as possible. To see how this model works, we will first consider the molecule BeCl_2 , which has the Lewis structure



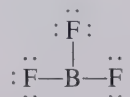
Note that there are two pairs of electrons around the beryllium atom. What arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsions? Clearly, the best arrangement places the pairs on opposite sides of the beryllium atom at 180 degrees from each other:



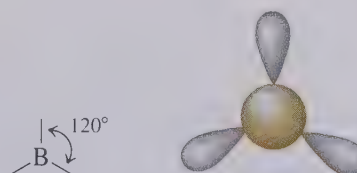
This is the maximum possible separation for two electron pairs. Once we have determined the optimal arrangement of the electron pairs around the central atom, we can specify the molecular structure of BeCl_2 , that is, the positions of the atoms. Since each electron pair on beryllium is shared with a chlorine atom, the molecule has a **linear structure** with a 180-degree bond angle:



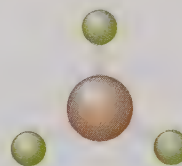
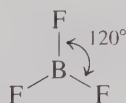
Next, let's consider BF_3 , which has the Lewis structure



Here the boron atom is surrounded by three pairs of electrons. What arrangement will minimize the repulsions? The electron pairs are farthest apart at angles of 120 degrees:

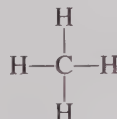


Since each of the electron pairs is shared with a fluorine atom, the molecular structure will be

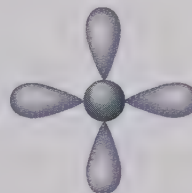


This is a planar (flat) and triangular molecule, which is commonly described as a **trigonal planar structure**.

Next, let's consider the methane molecule, which has the Lewis structure

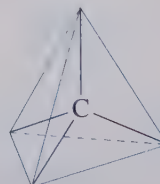
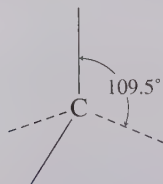


There are four pairs of electrons around the central carbon atom. What arrangement of these electron pairs best minimizes the repulsions? First, let's try a square planar arrangement:



The carbon atom and the electron pairs are centered in the plane of the paper, and the angles between the pairs are all 90 degrees.

Is there another arrangement with angles greater than 90 degrees that would put the electron pairs even farther away from each other? The answer is yes. The **tetrahedral structure** has angles of 109.5 degrees:



It can be shown that this is the maximum possible separation of four pairs around a given atom. This means that *whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally*.

Now that we have the electron-pair arrangement that gives the least repulsion, we can determine the positions of the atoms and thus the molecular structure of CH_4 . In methane, each of the four electron pairs is shared between the carbon atom and a hydrogen atom. Thus the hydrogen atoms are placed as in Fig. 8.14, and the molecule has a tetrahedral structure with the carbon atom at the center.

Recall that the main idea of the VSEPR model is to find the arrangement of electron pairs around the central atom that minimizes the repulsions. Then we can determine the molecular structure from knowing how the electron pairs are shared with the peripheral atoms. Use the following steps to predict the structure of a molecule using the VSEPR model.

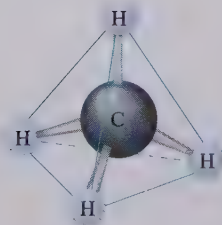


FIGURE 8.14

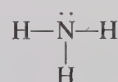
The molecular structure of methane. The tetrahedral arrangement of electron pairs produces a tetrahedral arrangement of hydrogen atoms.

Steps to Apply the VSEPR Model

- ➡ **1** Draw the Lewis structure for the molecule.
- ➡ **2** Count the electron pairs and arrange them in the way that minimizes repulsion (that is, put the pairs as far apart as possible).
- ➡ **3** Determine the positions of the atoms from the way the electron pairs are shared.
- ➡ **4** Determine the name of the molecular structure from the positions of the atoms.

We will predict the structure of ammonia (NH_3) using this stepwise approach.

- ➡ **1** Draw the Lewis structure:



- ➡ **2** Count the pairs of electrons and arrange them to minimize repulsions. The NH_3 molecule has four pairs of electrons: three bonding pairs and one nonbonding pair. From the discussion of the methane molecule, we know that the best arrangement of four electron pairs is a tetrahedral array, as shown in Fig. 8.15(a).

- ➡ **3** Determine the positions of the atoms. The three H atoms share electron pairs, as shown in Fig. 8.15(b).

- ➡ **4** Name the molecular structure. It is very important to recognize that the *name* of the molecular structure is always based on the *positions of the atoms*. The placement of the electron pairs determines the structure, but the name is based on the positions of the atoms. Thus it is incorrect to say that the NH_3 molecule is tetrahedral. It has a tetrahedral arrangement of electron pairs but not a tetrahedral arrangement of atoms. The molecular structure of ammonia is a **trigonal pyramid** (one side is different from the other three) rather than a tetrahedron, as shown in Fig. 8.15(c).



When four uniform balloons are tied together, they naturally form a tetrahedral shape.

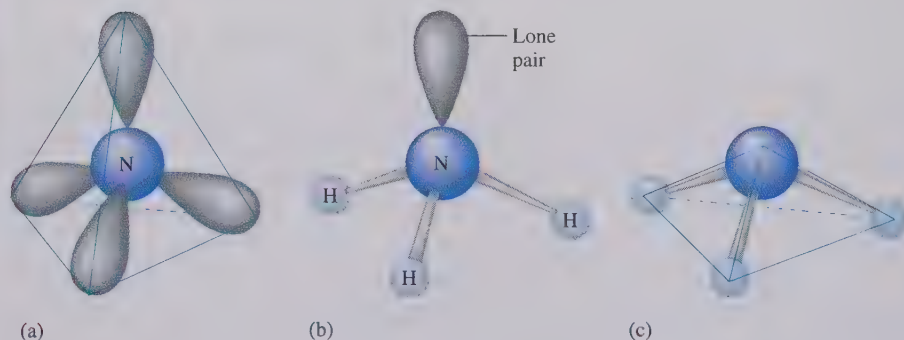
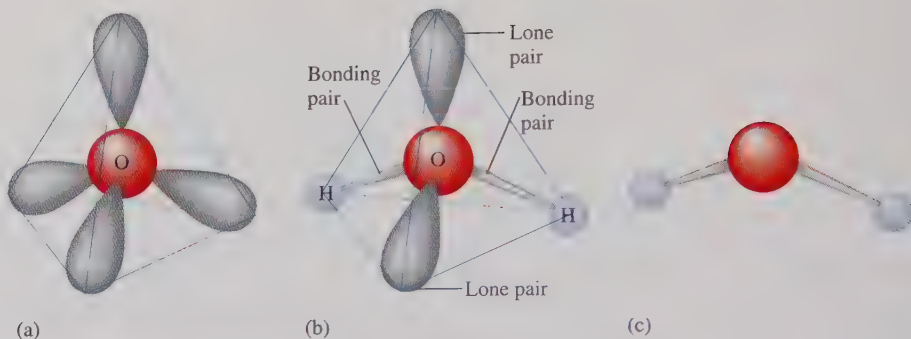


FIGURE 8.15

(a) The tetrahedral arrangement of electron pairs around the nitrogen atom in the ammonia molecule. (b) Three of the electron pairs around nitrogen are shared with hydrogen atoms as shown and one is a lone pair. Although the arrangement of *electron pairs* is tetrahedral, as in the methane molecule, the hydrogen atoms in the ammonia molecule occupy only three corners of the tetrahedron. A lone pair occupies the fourth corner. (c) Note that molecular geometry is trigonal pyramidal, not tetrahedral.

FIGURE 8.16

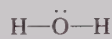
(a) The tetrahedral arrangement of the four electron pairs around oxygen in the water molecule. (b) Two of the electron pairs are shared between oxygen and the hydrogen atoms and two are lone pairs. (c) The V-shaped molecular structure of the water molecule.

**SAMPLE EXERCISE 8.11****Prediction of Molecular Structure I**

Describe the molecular structure of the water molecule.

SOLUTION

The Lewis structure for water is



There are four pairs of electrons: two bonding pairs and two nonbonding pairs. To minimize repulsions, these are best arranged in a tetrahedral array, as shown in Fig. 8.16(a). Although H_2O has a tetrahedral arrangement of electron pairs, it is not a tetrahedral molecule. The atoms in the H_2O molecule form a V shape, as shown in Fig. 8.16(b) and (c).

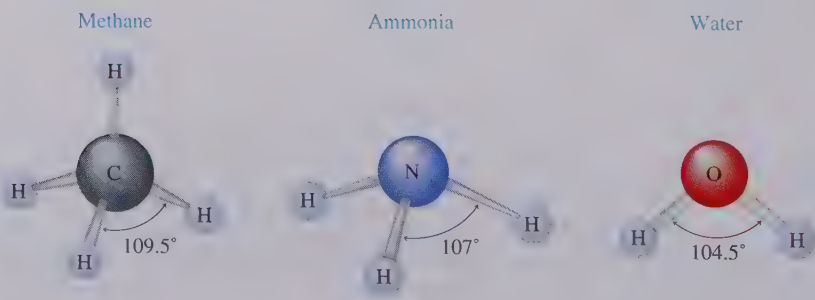
See Exercises 8.81 and 8.82.

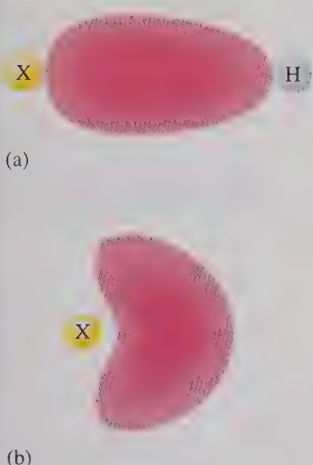
From Sample Exercise 8.11 we see that the H_2O molecule is V-shaped, or bent, because of the presence of the lone pairs. If no lone pairs were present, the molecule would be linear, the polar bonds would cancel, and the molecule would have no dipole moment. This would make water very different from the polar substance so familiar to us.

From the previous discussion we would predict that the $\text{H}-\text{X}-\text{H}$ bond angle (where X is the central atom) in CH_4 , NH_3 , and H_2O should be the tetrahedral angle of 109.5 degrees. Experimental studies, however, show that the actual bond angles are those given in Fig. 8.17. What significance do these results have for the VSEPR model? One possible point of view is that we should be pleased to have the observed angles so close to the tetrahedral angle. The opposite view is that the deviations are

FIGURE 8.17

The bond angles in the CH_4 , NH_3 , and H_2O molecules. Note that the bond angle between bonding pairs decreases as the number of lone pairs increases. Note that all of the angles in CH_4 are 109.5 degrees and all of the angles in NH_3 are 107 degrees.



**FIGURE 8.18**

(a) In a bonding pair of electrons, the electrons are shared by two nuclei. (b) In a lone pair, both electrons must be close to a single nucleus and tend to take up more of the space around that atom.

significant enough to require modification of the simple model so that it can more accurately handle similar cases. We will take the latter view.

Let us examine the following data:

	CH ₄	NH ₃	H ₂ O
Number of Lone Pairs	0	1	2
Bond Angle	109.5°	107°	104.5°

One interpretation of the trend observed here is that lone pairs require more space than bonding pairs; in other words, as the number of lone pairs increases, the bonding pairs are increasingly squeezed together.

This interpretation seems to make physical sense if we think in the following terms. A bonding pair is shared between two nuclei, and the electrons can be close to either nucleus. They are relatively confined between the two nuclei. A lone pair is localized on only one nucleus, and both electrons will be close only to that nucleus, as shown schematically in Fig. 8.18. These pictures help us understand why a lone pair may require more space near an atom than a bonding pair.

As a result of these observations, we make the following addition to the original postulate of the VSEPR model: *Lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs.*

So far we have considered cases with two, three, and four electron pairs around the central atom. These are summarized in Table 8.6. For five pairs of electrons, there are several possible choices. The one that produces minimum repulsion is a **trigonal bipyramid**. Note from Table 8.6 that this arrangement has two different angles, 90 degrees and 120 degrees. As the name suggests, the structure formed by this arrangement of pairs consists of two trigonal-based pyramids that share a common base. Six pairs of electrons can best be arranged around a given atom with 90-degree angles to form an **octahedral structure**, as shown in Table 8.6.

To use the VSEPR model to determine the geometric structures of molecules, you should memorize the relationships between the number of electron pairs and their best arrangement.

SAMPLE EXERCISE 8.12

Prediction of Molecular Structure II

When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl₅) is formed. In the gaseous and liquid states, this substance consists of PCl₅ molecules, but in the solid state it consists of a 1:1 mixture of PCl₄⁺ and PCl₆⁻ ions. Predict the geometric structures of PCl₅, PCl₄⁺, and PCl₆⁻.

SOLUTION

The Lewis structure for PCl₅ is shown. Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement (see Table 8.6). When the chlorine atoms are included, a trigonal bipyramidal molecule results:

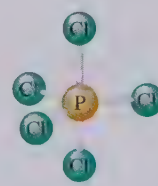
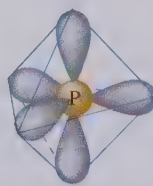
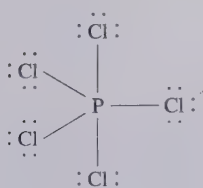
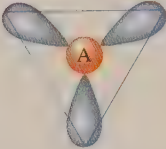
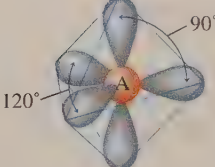
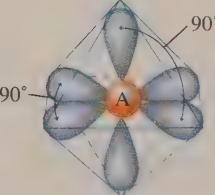
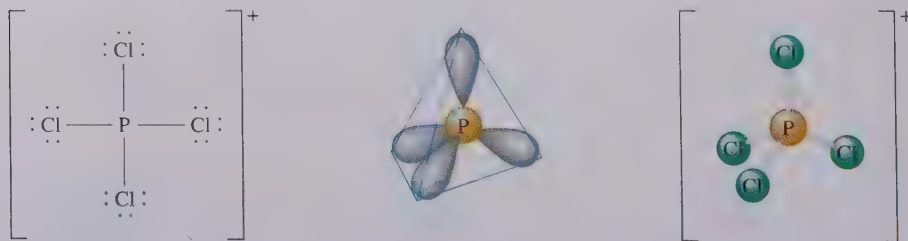


TABLE 8.6 Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

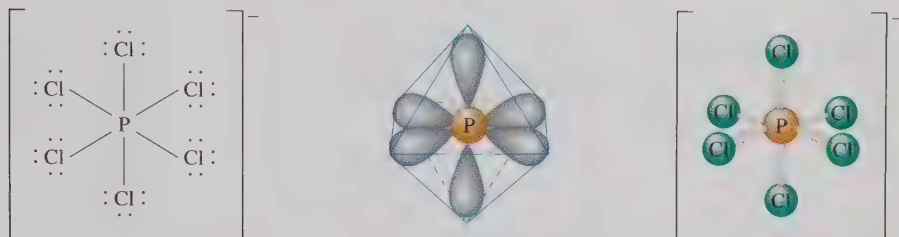
Number of Electron Pairs	Arrangement of Electron Pairs	Example
2	Linear 	
3	Trigonal planar 	
4	Tetrahedral 	
5	Trigonal bipyramidal 	
6	Octahedral 	

The Lewis structure for the PCl_4^+ ion ($5 + 4(7) - 1 = 32$ valence electrons) is shown below. There are four pairs of electrons surrounding the phosphorus atom in the PCl_4^+ ion, which requires a tetrahedral arrangement of the pairs. Since each pair is shared with a chlorine atom, a tetrahedral PCl_4^+ cation results.



The Lewis structure for PCl_6^- ($5 + 6(7) + 1 = 48$ valence electrons) is shown below. Since phosphorus is surrounded by six pairs of electrons, an octahedral arrange-

ment is required to minimize repulsions, as shown below in the center. Since each electron pair is shared with a chlorine atom, an octahedral PCl_6^- anion is predicted.



See Exercises 8.79, 8.80, 8.83, and 8.84.

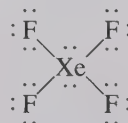
SAMPLE EXERCISE 8.13

Prediction of Molecular Structure III

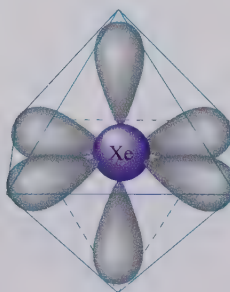
Because the noble gases have filled s and p valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called *inert gases* because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4). Predict its structure and whether it has a dipole moment.

SOLUTION

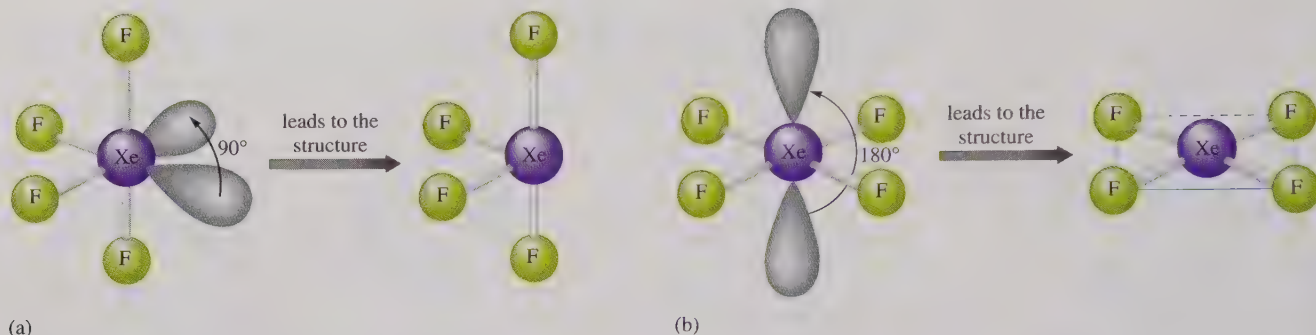
The Lewis structure for XeF_4 is



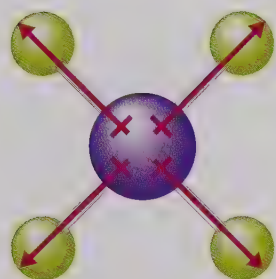
The xenon atom in this molecule is surrounded by six pairs of electrons, which means an octahedral arrangement.



The structure predicted for this molecule will depend on how the lone pairs and bonding pairs are arranged. Consider the two possibilities shown in Fig. 8.19. The bonding pairs are indicated by the presence of the fluorine atoms. Since the structure predicted differs in the two cases, we must decide which of these arrangements is preferable. The key is to look at the lone pairs. In the structure in part (a), the lone pair–lone pair angle is 90 degrees; in the structure in part (b), the lone pairs are separated by 180 degrees. Since lone pairs require more room than bonding pairs, a structure with two lone pairs at 90 degrees is unfavorable. Thus the arrangement in Fig. 8.19(b) is preferred, and the molecular structure is predicted to be square

**FIGURE 8.19**

Possible electron-pair arrangements for XeF_4 . Since arrangement (a) has lone pairs at 90 degrees from each other, it is less favorable than arrangement (b), where the lone pairs are at 180 degrees.

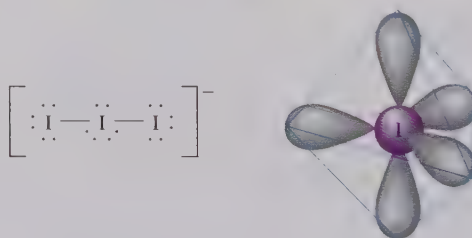


planar. Note that this molecule is *not* described as being octahedral. There is an *octahedral arrangement of electron pairs*, but the *atoms* form a **square planar structure**.

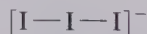
Although each Xe—F bond is polar (fluorine has a greater electronegativity than xenon), the square planar arrangement of these bonds causes the polarities to cancel. Thus XeF_4 has no dipole moment, as shown in the margin.

See Exercises 8.85 through 8.88.

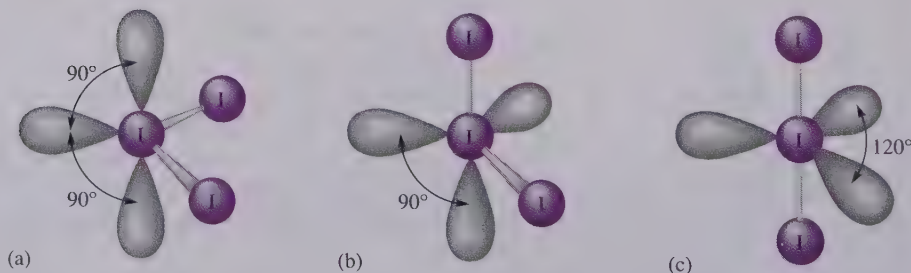
We can further illustrate the use of the VSEPR model for molecules or ions with lone pairs by considering the triiodide ion (I_3^-).



The central iodine atom has five pairs around it, which requires a trigonal bipyramidal arrangement. Several possible arrangements of lone pairs are shown in Fig. 8.20. Note that structures (a) and (b) have lone pairs at 90 degrees, whereas in (c) all lone pairs are at 120 degrees. Thus structure (c) is preferred. The resulting molecular structure for I_3^- is linear:

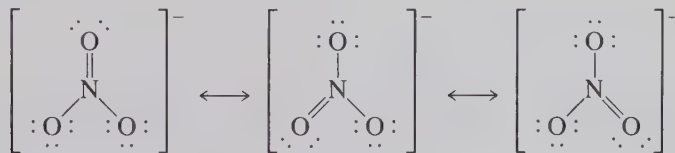
**FIGURE 8.20**

Three possible arrangements of the electron pairs in the I_3^- ion. Arrangement (c) is preferred because there are no 90-degree lone pair–lone pair interactions.

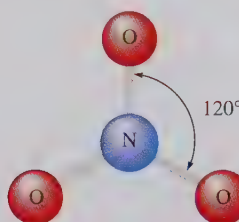


The VSEPR Model and Multiple Bonds

So far in our treatment of the VSEPR model we have not considered any molecules with multiple bonds. To see how these molecules are handled by this model, let's consider the NO_3^- ion, which requires three resonance structures to describe its electronic structure:



The NO_3^- ion is known to be planar with 120-degree bond angles:



This planar structure is the one expected for three pairs of electrons around a central atom, which means that *a double bond should be counted as one effective pair* in using the VSEPR model. This makes sense because the two pairs of electrons involved in the double bond are *not* independent pairs. Both the electron pairs must be in the space between the nuclei of the two atoms to form the double bond. In other words, the double bond acts as one center of electron density to repel the other pairs of electrons. The same holds true for triple bonds. This leads us to another general rule: *For the VSEPR model, multiple bonds count as one effective electron pair.*

The molecular structure of nitrate also shows us one more important point: *When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.* These rules are illustrated in Sample Exercise 8.14.

SAMPLE EXERCISE 8.14

Structures of Molecules with Multiple Bonds

Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?

SOLUTION

First, we must determine the Lewis structure for the SO_2 molecule, which has 18 valence electrons. The expected resonance structures are



To determine the molecular structure, we must count the electron pairs around the sulfur atom. In each resonance structure the sulfur has one lone pair, one pair in a single bond, and one double bond. Counting the double bond as one pair yields three

Chemical Structure and Communication: Semiochemicals

In this chapter we have stressed the importance of being able to predict the three-dimensional structure of a molecule. Molecular structure is important because of its effect on chemical reactivity. This is especially true in biological systems, where reactions must be efficient and highly specific. Among the hundreds of types of molecules in the fluids of a typical biological system, the appropriate reactants must find and react only with each other—they must be very discriminating. This specificity depends largely on structure. The molecules are constructed so that only the appropriate partners can approach each other in a way that allows reaction.

Another area where molecular structure is central is in the use of molecules as a means of communication. Examples of a chemical communication occur in humans in the conduction of nerve impulses across synapses, the control of the manufacture and storage of key chemicals in cells, and the senses of smell and taste. Plants and animals also use chemical communication. For example, ants lay down a chemical trail so that other ants can find a particular food supply. Ants also warn their fellow workers of approaching danger by emitting certain chemicals.

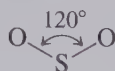
Molecules convey messages by fitting into appropriate receptor sites in a very specific way, which is determined



The queen bee secretes a chemical that prevents the worker bees from raising a competitive sovereign.

by their structure. When a molecule occupies a receptor site, chemical processes are stimulated that produce the appropriate response. Sometimes receptors can be fooled, as in the use of artificial sweeteners—molecules fit the sites on the taste buds that stimulate a “sweet” response in the brain, but they are not metabolized in the same way as natural sugars. Similar deception is useful in insect control. If an area is sprayed with synthetic female sex attractant molecules, the males of that species become so confused that mating does not occur.

effective pairs around the sulfur. According to Table 8.6, a trigonal planar arrangement is required, which yields a V-shaped molecule:



Thus the structure of the SO_2 molecule is expected to be V-shaped, with a 120-degree bond angle. The molecule has a dipole moment directed as shown:



Since the molecule is V-shaped, the polar bonds do not cancel.

See Exercises 8.89 and 8.90.

A *semiochemical* is a molecule that delivers a message between members of the same or different species of plant or animal. There are three groups of these chemical messengers: allomones, kairomones, and pheromones. Each is of great ecological importance.

An *allomone* is defined as a chemical that somehow gives adaptive advantage to the producer. For example, leaves of the black walnut tree contain a herbicide, juglone, that appears after the leaves fall to the ground. Juglone is not toxic to grass or certain grains, but it is effective against plants such as apple trees that would compete for the available water and food supplies.

Antibiotics are also allomones, since the microorganisms produce them to inhibit other species from growing near them.

Many plants produce bad-tasting chemicals to protect themselves from plant-eating insects and animals. The familiar compound nicotine deters animals from eating the tobacco plant. The millipede sends an unmistakable “back off” message by squirting a predator with benzaldehyde and hydrogen cyanide.

Defense is not the only use of allomones, however. Flowers use scent as a way to attract pollinating insects. Honeybees, for instance, are guided to alfalfa and flowers by a series of sweet-scented compounds.

Kairomones are chemical messengers that bring advantageous news to the receiver, and the floral scents are kairomones from the honeybees’ viewpoint. Many predators are guided by kairomones emitted by their food. For example, apple skins exude a chemical that attracts the codling moth larva. In some cases kairomones help the underdog. Certain marine mollusks can pick up the “scent” of their predators, the sea stars, and make their escape.

Pheromones are chemicals that affect receptors of the same species as the donor. That is, they are specific within a species. *Releaser pheromones* cause an immediate reaction in the receptor, and *primer pheromones* cause long-term effects. Examples of releaser pheromones are sex attractants of insects, generated in some species by the males and in others by the females. Sex pheromones also have been found in plants and mammals.

Alarm pheromones are highly volatile compounds (ones easily changed to a gas) released to warn of danger. Honeybees produce isoamyl acetate ($C_7H_{14}O_2$) in their sting glands. Because of its high volatility, this compound does not linger after the state of alert is over. Social behavior in insects is characterized by the use of *trail pheromones*, which are used to indicate a food source. Social insects such as bees, ants, wasps, and termites use these substances. Since trail pheromones are less volatile compounds, the indicators persist for some time.

Primer pheromones, which cause long-term behavioral changes, are harder to isolate and identify. One example, however, is the “queen substance” produced by queen honeybees. All the eggs in a colony are laid by one queen bee. If she is removed from the hive or dies, the worker bees are activated by the absence of the queen substance and begin to feed royal jelly to bee larvae so as to raise a new queen. The queen substance also prevents the development of the workers’ ovaries so that only the queen herself can produce eggs.

Many studies of insect pheromones are now under way in the hope that they will provide a method of controlling insects that is more efficient and safer than the current chemical pesticides.

It should be noted at this point that lone pairs that are oriented at least 120 degrees from other pairs do not produce significant distortions of bond angles. For example, the angle in the SO_2 molecule is actually quite close to 120 degrees. We will follow the general principle that *a 120-degree angle provides lone pairs with enough space so that distortions do not occur. Angles less than 120 degrees are distorted when lone pairs are present.*

Molecules Containing No Single Central Atom

So far we have considered molecules consisting of one central atom surrounded by other atoms. The VSEPR model can be readily extended to more complicated molecules, such as methanol (CH_3OH). This molecule is represented by the following Lewis structure:

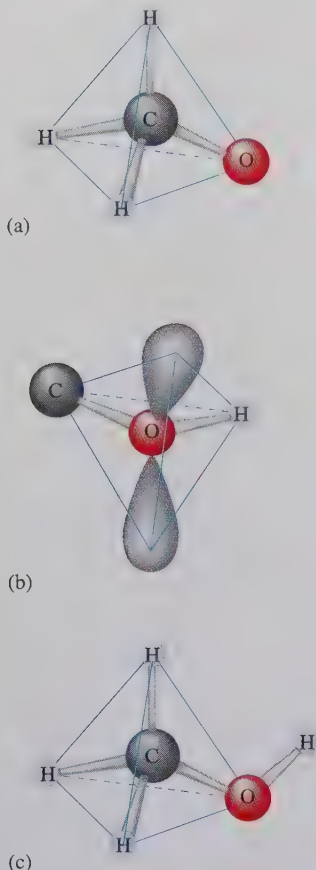
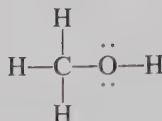


FIGURE 8.21

The molecular structure of methanol. (a) The arrangement of electron pairs and atoms around the carbon atom. (b) The arrangement of bonding and lone pairs around the oxygen atom. (c) The molecular structure.

The molecular structure can be predicted from the arrangement of pairs around the carbon and oxygen atoms. Note that there are four pairs of electrons around the carbon, which requires a tetrahedral arrangement, as shown in Fig. 8.21(a). The oxygen also has four pairs, which requires a tetrahedral arrangement. However, in this case the tetrahedron will be slightly distorted by the space requirements of the lone pairs [Fig. 8.21(b)]. The overall geometric arrangement for the molecule is shown in Fig. 8.21(c).

Summary of the VSEPR Model

The rules for using the VSEPR model to predict molecular structure follow:

- Determine the Lewis structure(s) for the molecule.
- For molecules with resonance structures, use any of the structures to predict the molecular structure.
- Sum the electron pairs around the central atom.
- In counting pairs, count each multiple bond as a single effective pair.
- The arrangement of the pairs is determined by minimizing electron-pair repulsions. These arrangements are shown in Table 8.6.
- Lone pairs require more space than bonding pairs do. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120 degrees.

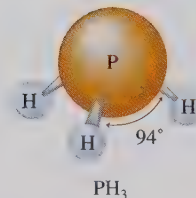
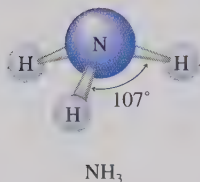
The VSEPR Model—How Well Does It Work?

The VSEPR model is very simple. There are only a few rules to remember, yet the model correctly predicts the molecular structures of most molecules formed from nonmetallic elements. Molecules of any size can be treated by applying the VSEPR model to each appropriate atom (those bonded to at least two other atoms) in the molecule. Thus we can use this model to predict the structures of molecules with hundreds of atoms. It does, however, fail in a few instances. For example, phosphine (PH_3), which has a Lewis structure analogous to that of ammonia,



would be predicted to have a molecular structure similar to that for NH_3 , with bond angles of approximately 107 degrees. However, the bond angles of phosphine are actually 94 degrees. There are ways of explaining this structure, but more rules have to be added to the model.

This again illustrates the point that simple models are bound to have exceptions. In introductory chemistry we want to use simple models that fit the majority of cases; we are willing to accept a few failures rather than complicate the model. The amazing thing about the VSEPR model is that such a simple model predicts correctly the structures of so many molecules.



Key Terms

Section 8.1

bond energy
ionic bonding
ionic compound
Coulomb's law
bond length
covalent bonding
polar covalent bond

Section 8.2

electronegativity

Section 8.3

dipolar
dipole moment

Section 8.4

isoelectronic ions

Section 8.5

lattice energy

Section 8.8

single bond
double bond
triple bond

Section 8.9

localized electron (LE) model
lone pair
bonding pair

Section 8.10

Lewis structure
duet rule
octet rule

For Review

Summary

Chemical bonds hold groups of atoms together. Bonding occurs when a group of atoms can lower its total energy by aggregating. Bonds can be classified into several types. In an ionic bond there is a transfer of electrons to form ions; in a covalent bond electrons are shared. Between these extremes, in a polar covalent bond electrons are shared unequally. The percent ionic character of the bond in a diatomic molecule XY can be defined as

$$\text{Percent ionic character} = \left(\frac{\text{measured dipole moment of } \text{X}-\text{Y}}{\text{calculated dipole moment } \text{X}^+\text{Y}^-} \right) \times 100\%$$

Electronegativity is defined as the relative ability of an atom in a molecule to attract the electrons shared in a bond. The electronegativity difference of the atoms involved in a bond determines the polarity of that bond. The spatial arrangement of polar bonds determines the overall polarity, or dipole moment, of a molecule.

Stable molecules usually contain atoms that have filled valence orbitals. Nonmetals bonding to each other achieve noble gas configurations in their valence orbitals by covalent bonding. A nonmetal and a representative-group metal achieve the same result by transferring electrons to form ions.

Ions have significantly different sizes from their parent atoms. Cations are smaller because the parent atom has lost electrons to become an ion. Anions, because they have more electrons than the parent atom, are larger. In general, ion size increases going down a group. Isoelectronic ions (having the same number of electrons) decrease in size with increasing Z values.

Lattice energy is the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid. Bond energy, the energy necessary to break a covalent bond, varies with the number of shared electron pairs. A single bond involves one electron pair; a double bond, two electron pairs; and a triple bond,

Section 8.12

resonance
resonance structure
formal charge

Section 8.13

molecular structure
valence shell electron-pair
repulsion (VSEPR) model
linear structure
trigonal planar structure
tetrahedral structure
trigonal pyramid
trigonal bipyramid
octahedral structure
square planar structure

three electron pairs. Bond energies can be used to calculate the enthalpy change for a reaction.

The Lewis structure of a molecule shows how the valence electrons are arranged among the atoms. The duet rule for hydrogen and the octet rule for second-row elements reflect the observation that atoms tend to fill their valence orbitals. Elements in the third row and beyond can exceed the octet rule because of the availability of empty *d* orbitals.

Sometimes more than one valid Lewis structure can be drawn for the same molecule, which is accounted for by the concept of resonance. The actual electronic structure is represented by the superposition of the resonance structures in such cases.

When several nonequivalent Lewis structures can be drawn for a molecule, formal charge is often used to choose the most appropriate structure(s). The VSEPR model is very useful in predicting the geometries of molecules formed from non-metals. The principal postulate of this model is that the structure around a given atom is determined by minimizing electron-pair repulsions.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Explain the electronegativity trends across a row and down a column of the periodic table. Compare these trends with those of ionization energies and atomic radii. How are they related?
2. The ionic compound AB is formed. The charges on the ions may be +1, -1; +2, -2; +3, -3; or even larger. What are the factors that determine the charge for an ion in an ionic compound?
3. Using only the periodic table, predict the most stable ion for Na, Mg, Al, S, Cl, K, Ca, and Ga. Arrange these from largest to smallest radius, and explain why the radius varies as it does. Compare your predictions with Fig. 8.7.
4. The bond energy for a C—H bond is about 413 kJ/mol in CH₄ but 380 kJ/mol in CHBr₃. Although these values are relatively close in magnitude, they are different. Explain why they are different. Does the fact that the bond energy is lower in CHBr₃ make any sense? Why?
5. Consider the following statement: "Because oxygen wants to have a negative two charge, the second electron affinity is more negative than the first." Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect statements and explain.
6. Which has the greater bond lengths: NO₂⁻ or NO₃⁻? Explain.
7. The following ions are best described with resonance structures. Draw the resonance structures, and using formal charge arguments, predict the best Lewis structure for each ion.

a. NCO⁻

b. CNO⁻

8. Would you expect the electronegativity of titanium to be the same in the species Ti, Ti²⁺, Ti³⁺, and Ti⁴⁺? Explain.
9. The second electron affinity values for both oxygen and sulfur are unfavorable (endothermic). Explain.
10. What is meant by a chemical bond? Why do atoms form bonds with each other? Why do some elements exist as molecules in nature instead of as free atoms?
11. Why are some bonds ionic and some covalent?
12. Does a Lewis structure tell which electrons come from which atoms? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

13. Explain the difference between the following pairs of terms.
 - a. electronegativity and electron affinity
 - b. covalent bond and polar covalent bond
 - c. polar covalent bond and ionic bond
14. Define the term *isoelectronic*. When comparing sizes of ions of elements in the same period in the periodic table, why is it advantageous to compare isoelectronic species?
15. Although the VSEPR model is correct in predicting that CH₄ is tetrahedral, NH₃ is pyramidal, and H₂O is bent, the model in its simplest form does not account for the fact that these molecules do not have exactly the same bond angles ($\angle$ HCH) is 109.5 degrees, as expected for a tetrahedron, but $\angle$ HNH is 107.3 degrees and $\angle$ HOH is 104.5 degrees). Explain these deviations from the tetrahedral angle.
16. Explain the terms *resonance* and *delocalized electrons*.

17. What two requirements should be satisfied for a molecule to be polar?
18. Give a rationalization for the octet rule in terms of orbitals.
19. Some plant fertilizer compounds are $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}_3(\text{PO}_4)_2$, K_2O , P_2O_5 , and KCl . Which of these compounds contain both ionic and covalent bonds?
20. Some of the important properties of ionic compounds are as follows:
 - i. low electrical conductivity as solids and high conductivity in solution or when molten
 - ii. relatively high melting and boiling points
 - iii. brittleness
 - iv. solubility in polar solvents
 How does the concept of ionic bonding discussed in this chapter account for these properties?

Exercises

In this section similar exercises are paired.

Chemical Bonds and Electronegativity

21. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements.
 - a. C, N, O
 - b. S, Se, Cl
 - c. Si, Ge, Sn
 - d. Tl, S, Ge
22. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements.
 - a. Na, K, Rb
 - b. B, O, Ga
 - c. F, Cl, Br
 - d. S, O, F
23. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.
 - a. C—F, Si—F, Ge—F
 - b. P—Cl or S—Cl
 - c. S—F, S—Cl, S—Br
 - d. Ti—Cl, Si—Cl, Ge—Cl
24. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.
 - a. C—H, Si—H, Sn—H
 - b. Al—Br, Ga—Br, In—Br, Tl—Br
 - c. C—O or Si—O
 - d. O—F or O—Cl
25. Repeat Exercises 21 and 23, this time using the values for the electronegativities of the elements given in Fig. 8.3. Are there differences in your answers?
26. Repeat Exercises 22 and 24, this time using the values for the electronegativities of the elements given in Fig. 8.3. Are there differences in your answers?
27. Hydrogen has an electronegativity value between boron and carbon and identical to phosphorus. With this in mind, rank the following bonds in order of decreasing polarity: P—H, O—H, N—H, F—H, C—H.
28. Rank the following bonds in order of increasing ionic character: N—O, Ca—O, C—F, Br—Br, K—F.

Ions and Ionic Compounds

29. Write electron configurations for the most stable ion formed by each of the elements Rb, Ba, Se, and I.
30. Write electron configurations for
 - a. the cations Mg^{2+} , K^+ , and Al^{3+} .
 - b. the anions N^{3-} , O^{2-} , F^- , and Te^{2-} .
31. Which of the following ions have noble gas electron configurations?
 - a. Fe^{2+} , Fe^{3+} , Sc^{3+} , Co^{3+}
 - b. Tl^+ , Te^{2-} , Cr^{3+}
 - c. Pu^{4+} , Ce^{4+} , Ti^{4+}
 - d. Ba^{2+} , Pt^{2+} , Mn^{2+}
32. What noble gas has the same electron configuration as each of the ions in the following compounds?
 - a. cesium sulfide
 - b. strontium fluoride
 - c. calcium nitride
 - d. aluminum bromide
33. Give three ions that are isoelectronic with neon. Place these ions in order of increasing size.
34. Give three ions that are isoelectronic with argon. Place these ions in order of increasing size.
35. For each of the following groups, place the atoms and/or ions in order of decreasing size.
 - a. Cu, Cu^+ , Cu^{2+}
 - b. Ni^{2+} , Pd^{2+} , Pt^{2+}
 - c. O, O^- , O^{2-}
 - d. La^{3+} , Eu^{3+} , Gd^{3+} , Yb^{3+}
 - e. Te^{2-} , I^- , Cs^+ , Ba^{2+} , La^{3+}
36. For each of the following groups, place the atoms and/or ions in order of decreasing size.
 - a. V, V^{2+} , V^{3+} , V^{5+}
 - b. Na^+ , K^+ , Rb^+ , Cs^+
 - c. Te^{2-} , I^- , Cs^+ , Ba^{2+}
 - d. P, P^- , P^{2-} , P^{3-}
 - e. O^{2-} , S^{2-} , Se^{2-} , Te^{2-}
37. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
 - a. Li and N
 - b. Ga and O
 - c. Rb and Cl
 - d. Ba and S

38. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
- Al and Cl
 - Na and O
 - Sr and F
 - Ca and P

39. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.
- NaCl, KCl
 - LiF, LiCl
 - Mg(OH)₂, MgO
 - Fe(OH)₂, Fe(OH)₃
 - NaCl, Na₂O
 - MgO, BaS

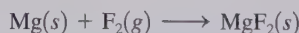
40. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.
- LiF, CsF
 - NaBr, NaI
 - BaCl₂, BaO
 - Na₂SO₄, CaSO₄
 - KF, K₂O
 - Li₂O, Na₂S

41. Use the following data to estimate ΔH_f° for sodium chloride.



Lattice energy	-786 kJ/mol
Ionization energy for Na	495 kJ/mol
Electron affinity of Cl	-349 kJ/mol
Bond energy of Cl ₂	239 kJ/mol
Enthalpy of sublimation for Na	109 kJ/mol

42. Use the following data to estimate ΔH_f° for magnesium fluoride.



Lattice energy	-3916 kJ/mol
First ionization energy of Mg	735 kJ/mol
Second ionization energy of Mg	1445 kJ/mol
Electron affinity of F	-328 kJ/mol
Bond energy of F ₂	154 kJ/mol
Enthalpy of sublimation of Mg	150 kJ/mol

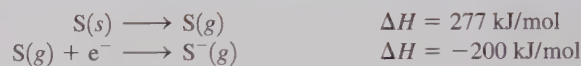
43. Consider the following energy changes:

	ΔH (kJ/mol)
$\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-$	735
$\text{Mg}^+(g) \rightarrow \text{Mg}^{2+}(g) + e^-$	1445
$\text{O}(g) + e^- \rightarrow \text{O}^-(g)$	-141
$\text{O}^-(g) + e^- \rightarrow \text{O}^{2-}(g)$	878

Magnesium oxide exists as $\text{Mg}^{2+}\text{O}^{2-}$ and not as Mg^+O^- . Explain.

44. Use the following data to estimate ΔH for the reaction $\text{S}^-(g) + e^- \longrightarrow \text{S}^{2-}(g)$. Include an estimate of uncertainty.

	ΔH_f°	Lattice Energy	I.E. of M	ΔH_{sub} of M
Li ₂ S	-500	-2472	520	161
Na ₂ S	-365	-2203	495	109
K ₂ S	-381	-2052	419	90
Rb ₂ S	-361	-1949	409	82
Cs ₂ S	-360	-1850	382	78



Assume that all values are known to ± 1 kJ/mol.

45. Rationalize the following lattice energy values:

Compound	Lattice Energy (kJ/mol)
CaSe	-2862
Na ₂ Se	-2130
CaTe	-2721
Na ₂ Te	-2095

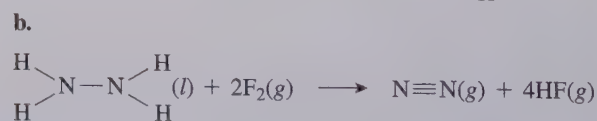
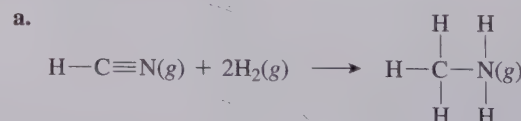
46. The lattice energies of FeCl₃, FeCl₂, and Fe₂O₃ are (in no particular order) -2631, -5359, and -14,774 kJ/mol. Match the appropriate formula to each lattice energy. Explain.

Bond Energies

47. Use bond energy values (Table 8.4) to estimate ΔH for each of the following reactions in the gas phase.

- $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
- $\text{N}\equiv\text{N} + 3\text{H}_2 \rightarrow 2\text{NH}_3$

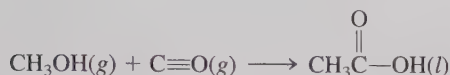
48. Use bond energy values (Table 8.4) to estimate ΔH for each of the following reactions.



49. Use bond energies (Table 8.4) to predict ΔH for the isomerization of methyl isocyanide to acetonitrile:



50. Acetic acid is responsible for the sour taste of vinegar. It can be manufactured using the following reaction:



Use tabulated values of bond energies (Table 8.4) to estimate ΔH for this reaction.

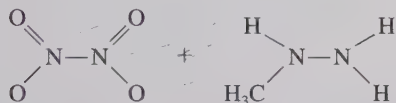
51. Use bond energies to predict ΔH for the combustion of ethanol:



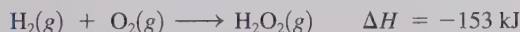
52. The space shuttle orbiter utilizes the oxidation of methyl hydrazine by dinitrogen tetroxide for propulsion:



Use bond energies to estimate ΔH for this reaction. The structures for the reactants are:

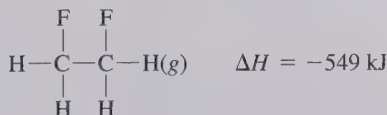
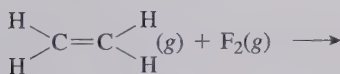


53. Consider the following reaction:



Given that the H_2 bond energy is 432 kJ/mol, the O_2 bond energy is 495 kJ/mol, and the OH bond energy is 467 kJ/mol, estimate the bond energy for the oxygen–oxygen single bond.

54. Consider the following reaction:



Estimate the carbon–fluorine bond energy given that the C–C bond energy is 347 kJ/mol, the C=C bond energy is 614 kJ/mol, and the F–F bond energy is 154 kJ/mol.

55. Compare your answers from parts a and b of Exercise 47 with ΔH values calculated for each reaction using standard enthalpies of formation in Appendix 4. Do enthalpy changes calculated from bond energies give a reasonable estimate of the actual values?
56. Compare your answer from Exercise 50 to the ΔH value calculated from standard enthalpies of formation in Appendix 4. Explain any discrepancies.

57. The standard enthalpies of formation for $\text{S}(g)$, $\text{F}(g)$, $\text{SF}_4(g)$, and $\text{SF}_6(g)$ are +278.8, +79.0, –775, and –1209 kJ/mol, respectively.

- Use these data to estimate the energy of an S–F bond.
- Compare your calculated values to the value given in Table 8.4. What conclusions can you draw?
- Why are the ΔH_f° values for $\text{S}(g)$ and $\text{F}(g)$ not equal to zero, since sulfur and fluorine are elements?

58. Use the following standard enthalpies of formation to estimate the N–H bond energy in ammonia: $\text{N}(g)$, 472.7 kJ/mol; $\text{H}(g)$, 216.0 kJ/mol; $\text{NH}_3(g)$, –46.1 kJ/mol. Compare your value to the one in Table 8.4.

59. The standard enthalpy of formation of $\text{NH}_3(g)$ is –46 kJ/mol. Use this and values for the $\text{N}\equiv\text{N}$ and $\text{H}-\text{H}$ bond energies to estimate the N–H bond energy. Compare this result with the value in Table 8.4.

60. The standard enthalpy of formation of $\text{N}_2\text{H}_4(g)$ is 95.4 kJ/mol. Use this along with the data and the result in Exercise 58 to estimate the N–N single bond energy. Compare this with the value in Table 8.4.

Lewis Structures and Resonance

61. Write Lewis structures that obey the octet rule for each of the following.

- | | | |
|--------------------|--------------------------|------------------|
| a. HCN | d. NH_4^+ | g. CO_2 |
| b. PH_3 | e. H_2CO | h. O_2 |
| c. CHCl_3 | f. SeF_2 | i. HBr |

Except for HCN and H_2CO , the first atom listed is the central atom. For HCN and H_2CO , carbon is the central atom.

62. Write Lewis structures that obey the octet rule for each of the following molecules and ions. (In each case the first atom listed is the central atom.)

- POCl_3 , SO_4^{2-} , XeO_4 , PO_4^{3-} , ClO_4^-
- NF_3 , SO_3^{2-} , PO_3^{3-} , ClO_3^-
- ClO_2^- , SCl_2 , PCl_2^-

- d. Considering your answers to parts a, b, and c, what conclusions can you draw concerning the structures of species containing the same number of atoms and the same number of valence electrons?

63. Write Lewis structures for the following molecules or ions, which have central atoms that do not obey the octet rule:



64. ClF_3 and BrF_3 are both used to fluorinate uranium to produce UF_6 in the processing and reprocessing of nuclear fuel. Write Lewis structures for ClF_3 and BrF_3 .

65. Write Lewis structures for the following. Show all resonance structures where applicable.

- NO_2^- , NO_3^- , N_2O_4 (N_2O_4 exists as $\text{O}_2\text{N}-\text{NO}_2$)
- OCN^- , SCN^- , N_3^- (Carbon is the central atom in OCN^- and SCN^- .)

66. Some of the important pollutants in the atmosphere are ozone (O_3), sulfur dioxide, and sulfur trioxide. Write Lewis structures for these three molecules. Show all resonance structures where applicable.
67. Benzene (C_6H_6) consists of a six-membered ring of carbon atoms with one hydrogen bonded to each carbon. Write Lewis structures for benzene, including resonance structures.
68. Borazine ($\text{B}_3\text{N}_3\text{H}_6$) has often been called “inorganic” benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms with one hydrogen bonded to each boron and nitrogen.
69. An important observation supporting the need for resonance in the localized electron model was that there are only three different structures of dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$). How does this fact support the need for the concept of resonance (see Exercise 67)?
70. Consider the following bond lengths:



In the CO_3^{2-} ion, all three C—O bonds have identical bond lengths of 136 pm. Why?

71. Place the species below in order of shortest to longest nitrogen–nitrogen bond.



(N_2F_4 exists as $\text{F}_2\text{N—NF}_2$, and N_2F_2 exists as FN—NF .)

72. Order the following species with respect to carbon–oxygen bond length (longest to shortest).



What is the order from the weakest to the strongest carbon–oxygen bond? (CH_3OH exists as $\text{H}_3\text{C—OH}$.)

Formal Charge

73. Write Lewis structures that obey the octet rule for the following species. Assign the formal charge for each central atom.
- POCl_3
 - SO_4^{2-}
 - ClO_4^-
 - PO_4^{3-}
 - SO_2Cl_2
 - XeO_4
 - ClO_3^-
 - NO_4^{3-}
74. Write Lewis structures for the species in Exercise 73 that involve minimum formal charges.

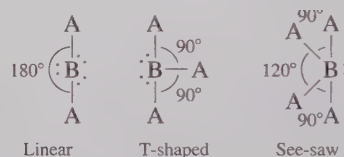
75. Write the Lewis structure for O_2F_2 (O_2F_2 exists as F—O—O—F). Assign oxidation states and formal charges to the atoms in O_2F_2 . This compound is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or

formal charges more useful in accounting for these properties of O_2F_2 ?

76. Oxidation of the cyanide ion produces the stable cyanate ion, OCN^- . The fulminate ion, CNO^- , on the other hand, is very unstable. Fulminate salts explode when struck; $\text{Hg}(\text{CNO})_2$ is used in blasting caps. Write the Lewis structures and assign formal charges for the cyanate and fulminate ions. Why is the fulminate ion so unstable? (C is the central atom in OCN^- and N is the central atom in CNO^- .)

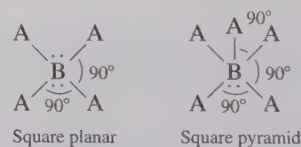
Molecular Structure and Polarity

77. Predict the molecular structure and bond angles for each molecule or ion in Exercises 61 and 65.
78. Predict the molecular structure and bond angles for each molecule or ion in Exercises 62 and 66.
79. There are several molecular structures based on the trigonal bipyramid geometry (see Table 8.6). Three such structures are



Which of the compounds in Exercises 63 and 64 have these molecular structures?

80. Two variations of the octahedral geometry (see Table 8.6) are illustrated below.



Which of the compounds in Exercise 63 have these molecular structures?

81. Predict the molecular structure (including bond angles) for each of the following.
- SeO_3
 - SeO_2
82. Predict the molecular structure (including bond angles) for each of the following.
- PCl_3
 - SCl_2
 - SiF_4
83. Predict the molecular structure (including bond angles) for each of the following. (See Exercises 79 and 80.)
- XeCl_2
 - ICl_3
 - TeF_4
 - PCl_5
84. Predict the molecular structure (including bond angles) for each of the following. (See Exercises 79 and 80.)

- a. ICl_5
- b. XeCl_4
- c. SeCl_6

85. Which of the molecules in Exercise 81 have dipole moments (are polar)?
86. Which of the molecules in Exercise 82 have dipole moments (are polar)?
87. Which of the molecules in Exercise 83 have dipole moments (are polar)?
88. Which of the molecules in Exercise 84 have dipole moments (are polar)?

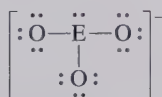
89. Write Lewis structures and predict the molecular structures of the following. (See Exercises 79 and 80.)

- a. OCl_2 , KrF_2 , BeH_2 , SO_2
- b. SO_3 , NF_3 , IF_3
- c. CF_4 , SeF_4 , KrF_4
- d. IF_5 , AsF_5

Which of these compounds are polar?

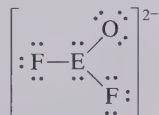
90. Write Lewis structures and predict whether each of the following is polar or nonpolar.
 - a. HOCN (exists as $\text{HO}-\text{CN}$)
 - b. COS
 - c. XeF_2
 - d. CF_2Cl_2
 - e. SeF_6
 - f. H_2CO (C is the central atom.)

91. Consider the following Lewis structure where E is an unknown element:



What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion.

92. Consider the following Lewis structure where E is an unknown element:



What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion. (See Exercises 79 and 80.)

93. The molecules BF_3 , CF_4 , CO_2 , PF_5 , and SF_6 are all nonpolar, even though they all contain polar bonds. Why?
94. Two different compounds have the formula XeF_2Cl_2 . Write Lewis structures for these two compounds, and describe how measurement of dipole moments might be used to distinguish between them.

Additional Exercises

95. Arrange the following in order of increasing radius and increasing ionization energy.

- a. N^+ , N , N^-
- b. Se , Se^- , Cl , Cl^+
- c. Br^- , Rb^+ , Sr^{2+}

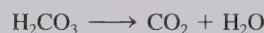
96. For each of the following, write an equation that corresponds to the energy given.

- a. lattice energy of NaCl
- b. lattice energy of NH_4Br
- c. lattice energy of MgS
- d. $\text{O}=\text{O}$ double bond energy beginning with $\text{O}_2(\text{g})$ as a reactant

97. Use bond energies (Table 8.4), values of electron affinities (Table 7.7), and the ionization energy of hydrogen (1312 kJ/mol) to estimate ΔH for each of the following reactions.

- a. $\text{HF}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{F}^-(\text{g})$
- b. $\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{Cl}^-(\text{g})$
- c. $\text{HI}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{I}^-(\text{g})$
- d. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{OH}^-(\text{g})$
(Electron affinity of $\text{OH}(\text{g}) = -180.$ kJ/mol.)

98. Write Lewis structures for CO_3^{2-} , HCO_3^- , and H_2CO_3 . When acid is added to an aqueous solution containing carbonate or bicarbonate ions, carbon dioxide gas is formed. We generally say that carbonic acid (H_2CO_3) is unstable. Use bond energies to estimate ΔH for the reaction (in the gas phase)



Specify a possible cause for the instability of carbonic acid.

99. Which member of the following pairs would you expect to be more energetically stable? Justify each choice.

- a. NaBr or NaBr_2
- b. ClO_4 or ClO_4^-
- c. SO_4 or XeO_4
- d. OF_4 or SeF_4

100. Lewis structures can be used to understand why some molecules react in certain ways. Write the Lewis structures for the reactants and products in the reactions described below.

- a. Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.
- b. Boron trifluoride accepts a pair of electrons from ammonia, forming BF_3NH_3 .

Give a possible explanation for why these two reactions occur.

101. Although both Br_3^- and I_3^- ions are known, the F_3^- ion has not been observed. Explain.

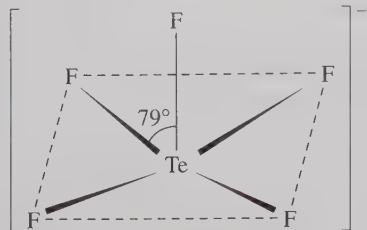
102. Carbon and sulfur form compounds with the formulas CS_2 and C_3S_2 . Draw Lewis structures and predict the shapes of these two compounds. C_3S_2 exists as $\text{S}-\text{C}-\text{C}-\text{S}$.

103. Refer back to Exercises 73 and 74. Would you make the same prediction for the molecular structure for each case using the Lewis structure obtained in Exercise 73 as compared with the one obtained in Exercise 74?

104. Which of the following molecules have dipole moments? For the molecules that are polar, indicate the polarity of each bond and the direction of the net dipole moment of the molecule.

- CH_2Cl_2 , CHCl_3 , CCl_4
- CO_2 , N_2O
- PH_3 , NH_3

105. The structure of TeF_5^- is



Draw a complete Lewis structure for TeF_5^- , and explain the distortion from the ideal square pyramidal structure. (See Exercise 80.)

Challenge Problems

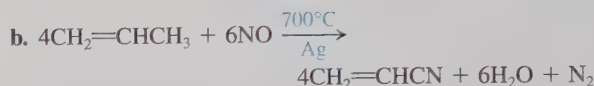
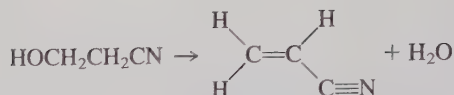
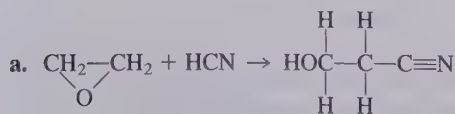
106. An alternative definition of electronegativity is

$$\text{Electronegativity} = \text{constant (I.E.} - \text{E.A.)}$$

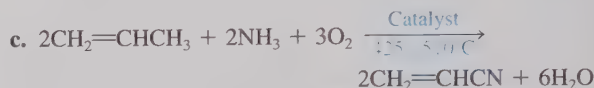
where I.E. is the ionization energy and E.A. is the electron affinity using the sign conventions of this book. Use data in Chapter 7 to calculate the (I.E. $-$ E.A.) term for F, Cl, Br, and I. Do these values show the same trend as the electronegativity values given in this chapter? The first ionization energies of the halogens are 1678, 1255, 1138, and 1007 kJ/mol, respectively. (Hint: Choose a constant so that the electronegativity of fluorine equals 4.0. Using this constant, calculate relative electronegativities for the other halogens and compare to values given in the text.)

107. The compound NF_3 is quite stable, but NCl_3 is very unstable (NCl_3 was first synthesized in 1811 by P.L. Dulong, who lost three fingers and an eye studying its properties). The compounds NBr_3 and NI_3 are unknown, although the explosive compound $\text{NI}_3 \cdot \text{NH}_3$ is known. Account for the instability of these halides of nitrogen.

108. Three processes that have been used for the industrial manufacture of acrylonitrile (CH_2CHCN), an important chemical used in the manufacture of plastics, synthetic rubber, and fibers, are shown below. Use bond energy values (Table 8.4) to estimate ΔH for each of the reactions.

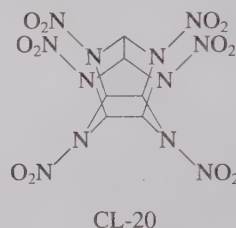


The nitrogen–oxygen bond energy in nitric oxide (NO) is 630. kJ/mol.



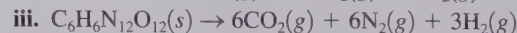
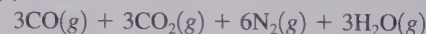
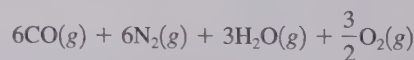
d. Is the elevated temperature noted in parts b and c needed to provide energy to endothermic reactions?

109. The compound hexaazaisowurtzitane is the highest-energy explosive known (*C & E News*, Jan. 17, 1994, p. 26). The compound, also known as CL-20, was first synthesized in 1987. The method of synthesis and detailed performance data are still classified because of CL-20's potential military application in rocket boosters and in warheads of "smart" weapons. The structure of CL-20 is



In such shorthand structures, each point where lines meet represents a carbon atom. In addition, the hydrogens attached to the carbon atoms are omitted; each of the six carbon atoms has one hydrogen atom attached. Finally, assume that the two O atoms in the NO_2 groups are attached to N with one single bond and one double bond.

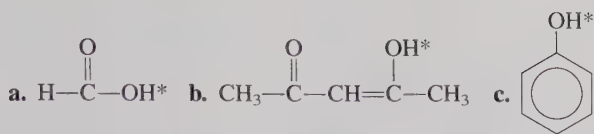
Three possible reactions for the explosive decomposition of CL-20 are



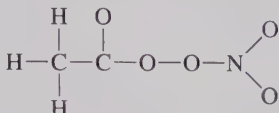
a. Use bond energies to estimate ΔH for these three reactions.

b. Which of the above reactions releases the largest amount of energy per kilogram of CL-20?

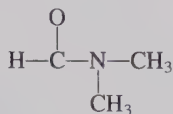
110. Many times extra stability is characteristic of a molecule or ion in which resonance is possible. How could this be used to explain the acidities of the following compounds? (The acidic hydrogen is marked by an asterisk.) Part c shows resonance in the C_6H_5 ring.



111. Peroxacetyl nitrate, or PAN, is present in photochemical smog. Draw Lewis structures (including resonance forms) for PAN. The skeletal arrangement is



112. Draw a Lewis structure for the *N,N*-dimethylformamide molecule. The skeletal structure is



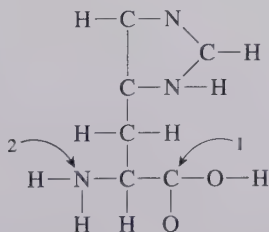
Various types of evidence lead to the conclusion that there is some double bond character to the C—N bond. Draw one or more resonance structures that support this observation.

113. Predict the molecular structure for each of the following. (See Exercises 79 and 80.)

- a. BrFl_2
b. XeO_2F_2
c. $\text{TeF}_2\text{Cl}_3^-$

For each formula there are at least two different structures that can be drawn using the same central atom. Draw all possible structures for each formula.

114. The study of carbon-containing compounds and their properties is called *organic chemistry*. Besides carbon atoms, organic compounds also can contain hydrogen, oxygen, and nitrogen atoms (as well as other types of atoms). A common trait of simple organic compounds is to have Lewis structures where all atoms have a formal charge of zero. Consider the following incomplete Lewis structure for an organic compound called *histidine* (an amino acid, which is the building block of all proteins found in our bodies):



Draw a complete Lewis structure for histidine in which all atoms have a formal charge of zero. What should be the approximate bond angles about the carbon atom labeled 1 and the nitrogen atom labeled 2?

115. Nitrous oxide (N_2O) has three possible Lewis structures:



Given the following bond lengths,

N—N	167 pm	N=O	115 pm
N=N	120 pm	N—O	147 pm
N≡N	110 pm		

rationalize the observations that the N—N bond length in N_2O is 112 pm and that the N—O bond length is 119 pm. Assign formal charges to the resonance structures for N_2O . Can you eliminate any of the resonance structures on the basis of formal charges? Is this consistent with observation?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

116. Identify the five compounds of H, N, and O described below. For each compound, write a Lewis structure that is consistent with the information given.

- All the compounds are electrolytes, although not all of them are strong electrolytes. Compounds C and D are ionic and compound B is covalent.
- Nitrogen occurs in its highest possible oxidation state in compounds A and C; nitrogen occurs in its lowest possible oxidation state in compounds C, D, and E. The formal charge on both nitrogens in compound C is +1; the formal charge on the only nitrogen in compound B is 0.
- Compounds A and E exist in solution. Both solutions give off gases. Commercially available concentrated solutions of compound A are normally 16 M. The commercial, concentrated solution of compound E is 15 M.
- Commercial solutions of compound E are labeled with a misnomer that implies that a binary, gaseous compound of nitrogen and hydrogen has reacted with water to produce ammonium ions and hydroxide ions. Actually, this reaction occurs to only a slight extent.
- Compound D is 43.7% N and 50.0% O by mass. If compound D were a gas at STP, it would have a density of 2.86 g/L.
- A formula unit of compound C has one more oxygen than a formula unit of compound D. Compounds C and A have one ion in common when compound A is acting as a strong electrolyte.
- Solutions of compound C are weakly acidic; solutions of compound A are strongly acidic; solutions of compounds B and E are basic. The titration of 0.726 g of compound B requires 21.98 mL of 1.000 M HCl for complete neutralization.

 Media Activities

1. Work through the Formation of Ionic Compounds Understanding Concepts activity on the student CD. Complete the exercises until you are proficient at predicting formulas.

a. In the exercises, the charges of the ions are given. However, you should be able to predict the cation charges for some of the metal ions given and the anion charges for all of the nonmetal ions given. Review Table 8.3 to figure out how and why. Do Exercises 8.37 and 8.38 in the text to reinforce predicting ion charges.

b. How is the size of a cation related to the size of the neutral atom? Explain. How is the size of an anion related to the size of the neutral atom? What is an isoelectronic series of ions? What determines the size trend in an isoelectronic series? Practice placing ions in order of increasing size by doing Exercises 8.33 and 8.35 in the text.

2. At the heart of the localized electron (LE) model is drawing Lewis structures. You must be proficient at drawing correct Lewis structures in order to apply the LE model. This takes practice.

a. Once you feel comfortable drawing Lewis structures, open the VSEPR Theory of Molecular Structure Understanding Concepts activity on the student CD and skip directly to the exercises. For now, just concentrate on drawing correct Lewis structures. For each molecule or ion, draw the Lewis structure, then check your answer by clicking Hint: Examine Lewis Structure.

b. The Lewis structures in the Hint are incorrect for CO_2 , NO_2^- , O_3 , and SO_2 . What was wrong with the answers? NO_2^- , O_3 , and SO_2 all exhibit resonance. What is resonance

and how many resonance structures can be drawn for these three species? How many resonance structures can be drawn for CO_3^{2-} ? for SO_3 ?

c. There were several exceptions to the octet rule in the various choices. Which two second-row atoms often have fewer than eight electrons? Which elements sometimes have more than eight electrons?

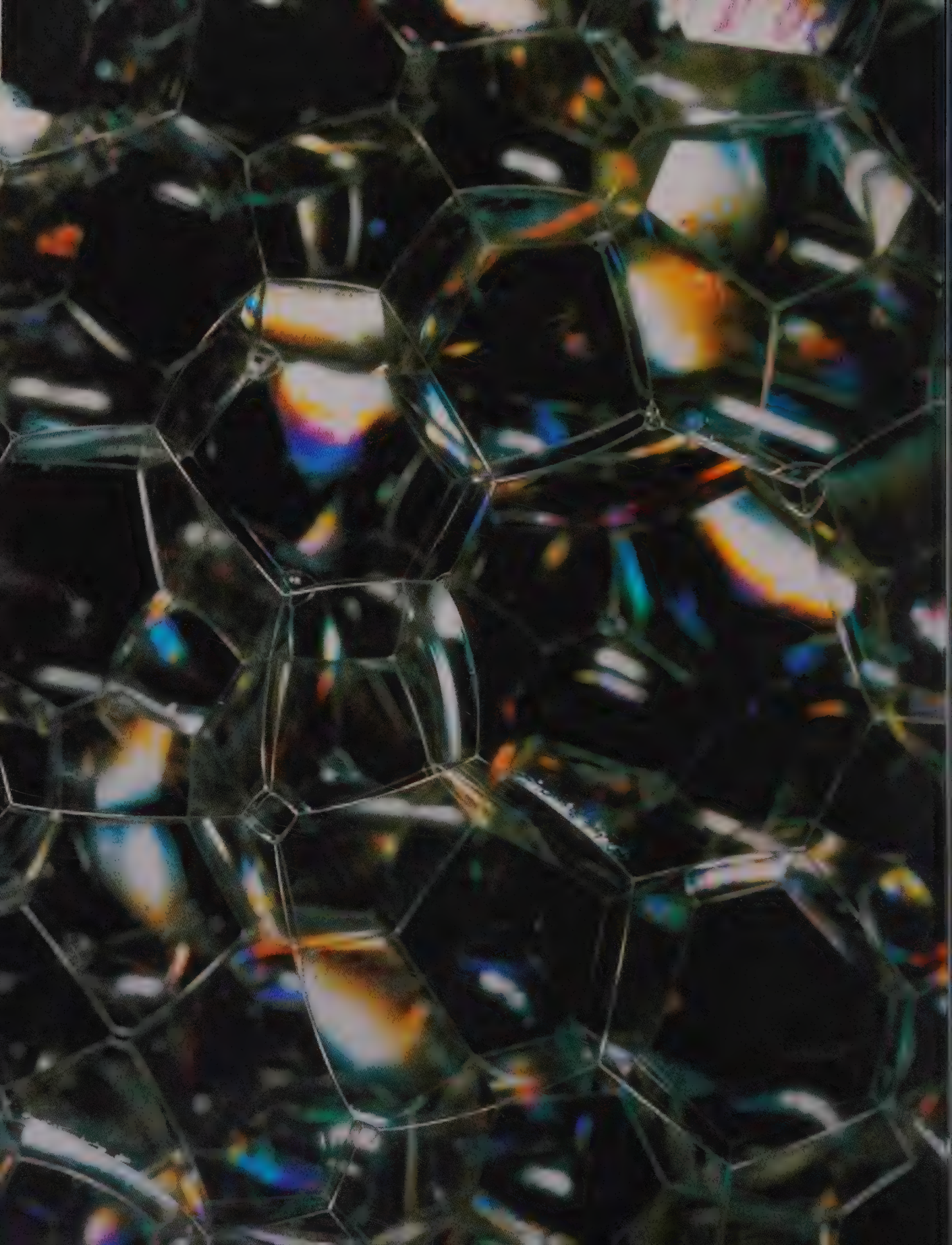
3. a. Open the VSEPR Theory of Molecular Structure Understanding Concepts activity on the student CD. The table at the end of the example offers an excellent review of all the possible shapes. Review the table to make sure that you can list approximate bond angles present for each shape. For example, see-saw shaped molecules would exhibit approximate 90-degree and 120-degree bond angles, where T-shaped molecules would exhibit approximate 90-degree bond angles (120-degree bond angles no longer exist). Bond angles are sometimes smaller than predicted from the VSEPR model. Explain this phenomenon.

b. Once you are comfortable with the various shapes in the table, go to the exercises in the activity and predict the shape for every example available. This is an excellent review exercise on shapes. While going through each molecule/ion, also predict the approximate bond angles.

4. Test your understanding of Chapter 8 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Covalent Bonding: Orbitals

In Chapter 8 we discussed the fundamental concepts of bonding and introduced the most widely used simple model for covalent bonding: the localized electron model. We saw the usefulness of a bonding model as a means for systematizing chemistry by allowing us to look at molecules in terms of individual bonds. We also saw that molecular structure can be predicted by minimizing electron-pair repulsions. In this chapter we will examine bonding models in more detail, particularly focusing on the role of orbitals.

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- 9.1 Hybridization and the Localized Electron Model**
 - sp^3 Hybridization
 - sp^2 Hybridization
 - sp Hybridization
 - dsp^3 Hybridization
 - d^2sp^3 Hybridization
 - The Localized Electron Model: A Summary
- 9.2 The Molecular Orbital Model**
 - Bond Order
- 9.3 Bonding in Homonuclear Diatomic Molecules**
 - Paramagnetism
- 9.4 Bonding in Heteronuclear Diatomic Molecules**
- 9.5 Combining the Localized Electron and Molecular Orbital Models**

9.1 Hybridization and the Localized Electron Model

As we saw in Chapter 8, the localized electron model views a molecule as a collection of atoms bound together by sharing electrons between their atomic orbitals. The arrangement of valence electrons is represented by the Lewis structure (or structures, where resonance occurs), and the molecular geometry can be predicted from the VSEPR model. In this section we will describe the atomic orbitals used to share electrons and hence to form the bonds.

Visualization: sp^3 Hybridization

The valence orbitals are the orbitals associated with the highest principal quantum level that contains electrons on a given atom.

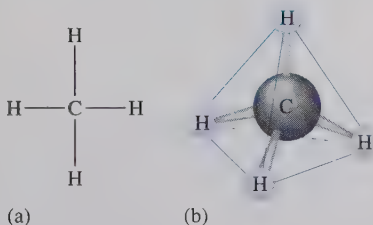


FIGURE 9.1

(a) The Lewis structure of the methane molecule. (b) The tetrahedral molecular geometry of the methane molecule.

Hybridization is a modification of the localized electron model to account for the observation that atoms often seem to use special atomic orbitals in forming molecules.

sp^3 hybridization gives a tetrahedral set of orbitals.

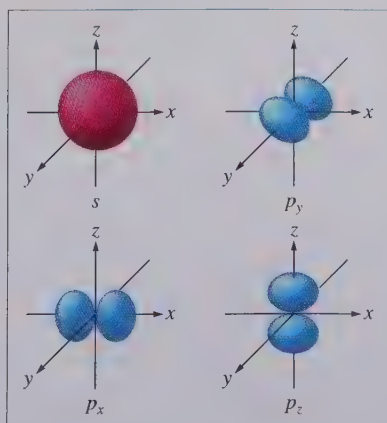


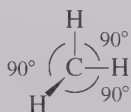
FIGURE 9.2

The valence orbitals on a free carbon atom: $2s$, $2p_x$, $2p_y$, and $2p_z$.

 sp^3 Hybridization

Let us reconsider the bonding in methane, which has the Lewis structure and molecular geometry shown in Fig. 9.1. In general, we assume that bonding involves only the valence orbitals. This means that the hydrogen atoms in methane use $1s$ orbitals. The valence orbitals of a carbon atom are the $2s$ and $2p$ orbitals shown in Fig. 9.2. In thinking about how carbon can use these orbitals to bond to the hydrogen atoms, we can see two related problems:

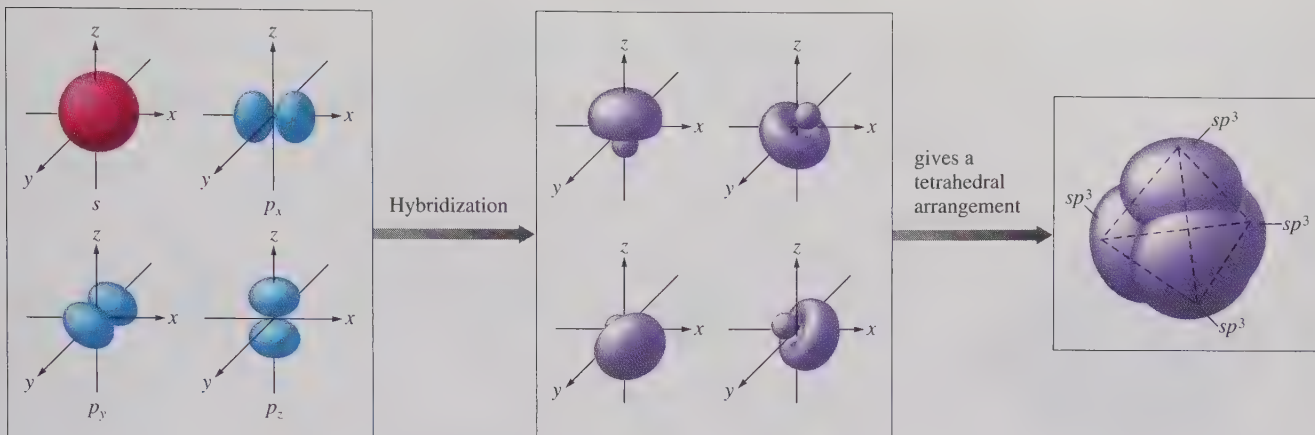
1. Using the $2p$ and $2s$ atomic orbitals will lead to two different types of C—H bonds: (a) those from the overlap of a $2p$ orbital of carbon and a $1s$ orbital of hydrogen (there will be three of these) and (b) those from the overlap of a $2s$ orbital of carbon and a $1s$ orbital of hydrogen (there will be one of these). This is a problem because methane is known to have four identical C—H bonds.
2. Since the carbon $2p$ orbitals are mutually perpendicular, we might expect the three C—H bonds formed with these orbitals to be oriented at 90-degree angles:



However, the methane molecule is known by experiment to be tetrahedral with bond angles of 109.5 degrees.

This analysis leads to one of two conclusions: Either the simple localized electron model is wrong or carbon adopts a set of atomic orbitals other than its “native” $2s$ and $2p$ orbitals to bond to the hydrogen atoms in forming the methane molecule. The second conclusion seems more reasonable. The $2s$ and $2p$ orbitals present on an *isolated* carbon atom may not be the best set of orbitals for bonding; a new set of atomic orbitals might better serve the carbon atom in forming molecules. To account for the known structure of methane, it makes sense to assume that the carbon atom has four equivalent atomic orbitals, arranged tetrahedrally. In fact, such a set of orbitals can be obtained quite readily by combining the carbon $2s$ and $2p$ orbitals, as shown schematically in Fig. 9.3. This mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization**. The four new orbitals are called sp^3 orbitals because they are formed from one $2s$ and three $2p$ orbitals (s^1p^3). We say that the carbon atom undergoes sp^3 hybridization or is sp^3 hybridized. The four sp^3 orbitals are identical in shape, each one having a large lobe and a small lobe (see Fig. 9.4). The four orbitals are oriented in space so that the large lobes form a tetrahedral arrangement, as shown in Fig. 9.3.

The hybridization of the carbon $2s$ and $2p$ orbitals also can be represented by an orbital energy-level diagram, as shown in Fig. 9.5. Note that electrons have been omitted because we do not need to be concerned with the electron arrangements on the individual atoms—it is the total number of electrons and the arrangement of these electrons in the *molecule* that are important. We are assuming that carbon’s atomic orbitals are rearranged to accommodate the best electron arrangement for the molecule as a whole. The new sp^3 atomic orbitals on carbon are used to share electron pairs with the $1s$ orbitals from the four hydrogen atoms, as shown in Fig. 9.6 on page 416.

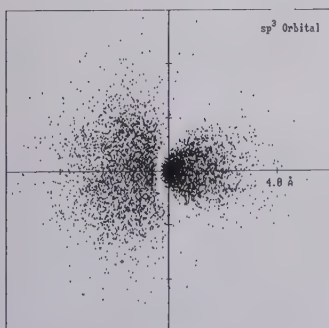
**FIGURE 9.3**

The “native” $2s$ and three $2p$ atomic orbitals characteristic of a free carbon atom are combined to form a new set of four sp^3 orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

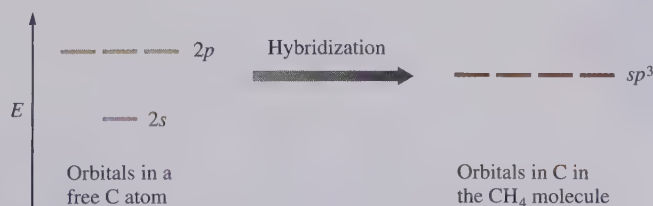
At this point let’s summarize the bonding in the methane molecule. The experimentally known structure of this molecule can be explained if we assume that the carbon atom adopts a special set of atomic orbitals. These new orbitals are obtained by combining the $2s$ and the three $2p$ orbitals of the carbon atom to produce four identically shaped orbitals that are oriented toward the corners of a tetrahedron and are used to bond to the hydrogen atoms. Thus the four sp^3 orbitals on carbon in methane are postulated to account for its known structure.

Remember this principle: *Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.*

It is really not surprising that an atom in a molecule might adopt a different set of atomic orbitals (called **hybrid orbitals**) from those it has in the free state. It does not seem unreasonable that to achieve minimum energy, an atom uses one set of atomic orbitals in the free state and a different set in a molecule. This is consistent with the idea that a molecule is more than simply a sum of its parts. What the atoms in a molecule were like before the molecule was formed is not as important as how the electrons are best arranged in the molecule. Therefore, this model assumes that the individual atoms respond as needed to achieve the minimum energy for the molecule.

**FIGURE 9.4**
Cross section of an sp^3 orbital.

(Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC2402; printed with permission.)

**FIGURE 9.5**

An energy-level diagram showing the formation of four sp^3 orbitals.

SAMPLE EXERCISE 9.1

The Localized Electron Model I

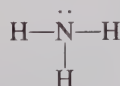
Describe the bonding in the ammonia molecule using the localized electron model.

SOLUTION

A complete description of the bonding involves three steps:

1. Writing the Lewis structure
2. Determining the arrangement of electron pairs using the VSEPR model
3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule

The Lewis structure for NH_3 is

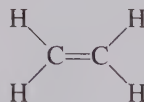


The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of sp^3 hybrid orbitals is obtained by combining the $2s$ and three $2p$ orbitals. In the NH_3 molecule three of the sp^3 orbitals are used to form bonds to the three hydrogen atoms, and the fourth sp^3 orbital holds the lone pair, as shown in Fig. 9.7.

See Exercise 9.11.

 sp^2 Hybridization

Ethylene (C_2H_4) is an important starting material in the manufacture of plastics. The C_2H_4 molecule has 12 valence electrons and the following Lewis structure:



We saw in Chapter 8 that a double bond acts as one effective pair, so in the ethylene molecule each carbon is surrounded by three effective pairs. This requires a trigonal planar arrangement with bond angles of 120 degrees. What orbitals do the carbon atoms in this molecule employ? The molecular geometry requires a set of orbitals in one plane at angles of 120 degrees. Since the $2s$ and $2p$ valence orbitals of carbon do not have the required arrangement, we need a set of hybrid orbitals.

The sp^3 orbitals we have just considered will not work because they are at angles of 109.5 degrees rather than the required 120 degrees. In ethylene the carbon atom must hybridize in a different manner. A set of three orbitals arranged at 120-degree angles in the same plane can be obtained by combining one s orbital and two p orbitals, as shown in Fig. 9.8. The orbital energy-level diagram for this arrangement is shown in Fig. 9.9. Since one $2s$ and two $2p$ orbitals are used to form these hybrid orbitals, this is called **sp^2 hybridization**. Note from Fig. 9.8 that the plane of the sp^2 hybridized orbitals is determined by which p orbitals are used. Since in this case we have arbitrarily decided to use the p_x and p_y orbitals, the hybrid orbitals are centered in the xy plane.

In forming the sp^2 orbitals, one $2p$ orbital on carbon has not been used. This

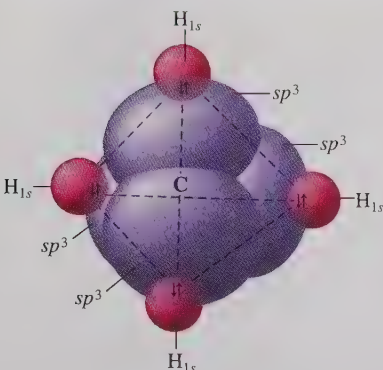


FIGURE 9.6

The tetrahedral set of four sp^3 orbitals of the carbon atom are used to share electron pairs with the four $1s$ orbitals of the hydrogen atoms to form the four equivalent C—H bonds. This accounts for the known tetrahedral structure of the CH_4 molecule.

A double bond acts as one effective electron pair.

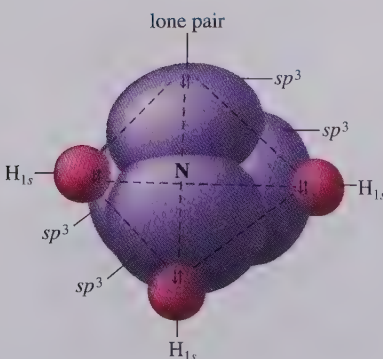
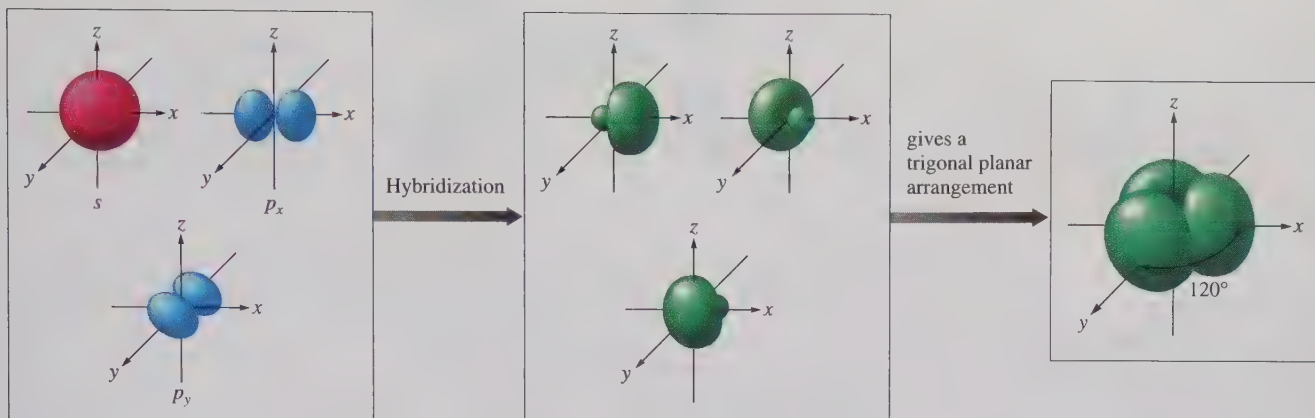


FIGURE 9.7

The nitrogen atom in ammonia is sp^3 hybridized.

**FIGURE 9.8**

The hybridization of the s , p_x , and p_y atomic orbitals results in the formation of three sp^2 orbitals centered in the xy plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

sp^2 hybridization gives a trigonal planar arrangement of atomic orbitals.

Note in Fig. 9.10 and the figures that follow that the orbital lobes are artificially narrowed to more clearly show their relative orientations.



Visualization: sp^2 Hybridization

remaining p orbital (p_z) is oriented perpendicular to the plane of the sp^2 orbitals, as shown in Fig. 9.10.

Now we will see how these orbitals can be used to account for the bonds in ethylene. The three sp^2 orbitals on each carbon can be used to share electrons, as shown in Fig. 9.11. In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms. This type of covalent bond is called a **sigma (σ) bond**. In the ethylene molecule, the σ bonds are formed using sp^2 orbitals on each carbon atom and the $1s$ orbital on each hydrogen atom.

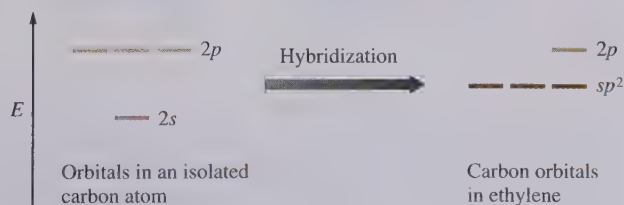
How can we explain the double bond between the carbon atoms? In the σ bond the electron pair occupies the space between the carbon atoms. The second bond must therefore result from sharing an electron pair in the space *above and below* the σ bond. This type of bond can be formed using the $2p$ orbital perpendicular to the sp^2 hybrid orbitals on each carbon atom (refer to Fig. 9.10). These parallel p orbitals can share an electron pair, which occupies the space above and below a line joining the atoms, to form a **pi (π) bond**, as shown in Fig. 9.12.

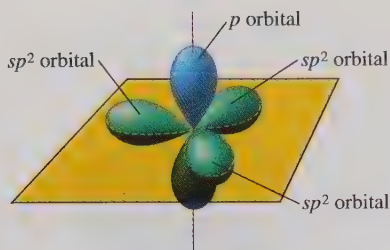
Note that σ bonds are formed from orbitals whose lobes point toward each other, but π bonds result from parallel orbitals. A *double bond always consists of one σ bond*, where the electron pair is located directly between the atoms, *and one π bond*, where the shared pair occupies the space above and below the σ bond.

We can now completely specify the orbitals that this model assumes are used to form the bonds in the ethylene molecule. As shown in Fig. 9.13, the carbon atoms use sp^2 hybrid orbitals to form the σ bonds to the hydrogen atoms and to each other, and they use p orbitals to form the π bond with each other. Note that we have accounted fully for the Lewis structure of ethylene with its carbon–carbon double bond and carbon–hydrogen single bonds.

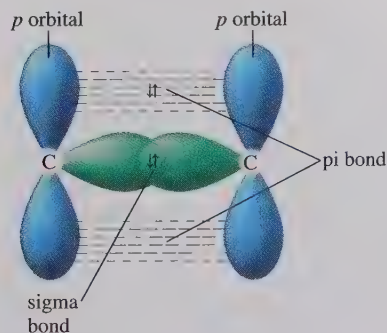
FIGURE 9.9

An orbital energy-level diagram for sp^2 hybridization. Note that one p orbital remains unchanged.



**FIGURE 9.10**

When an s and two p orbitals are mixed to form a set of three sp^2 orbitals, one p orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with narrowed lobes to show their orientations more clearly.

**FIGURE 9.12**

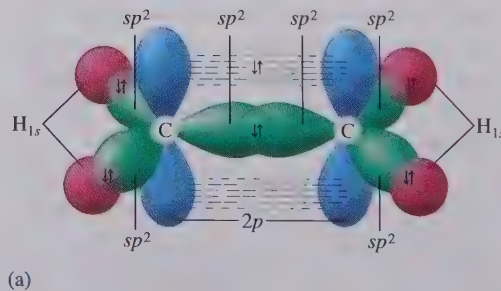
A carbon-carbon double bond consists of a σ bond and a π bond. In the σ bond the shared electrons occupy the space directly between the atoms. The π bond is formed from the unhybridized p orbitals on the two carbon atoms. In a π bond the shared electron pair occupies the space above and below a line joining the atoms.



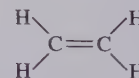
Visualization: sp Hybridization

FIGURE 9.13

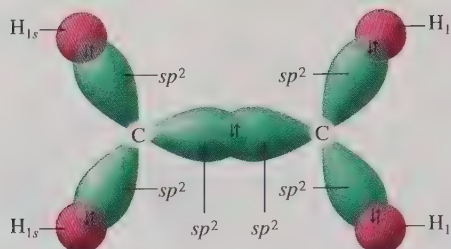
(a) The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene.



(a)



(b)

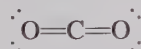
**FIGURE 9.11**

The σ bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

This example illustrates an important general principle of this model: *Whenever an atom is surrounded by three effective pairs, a set of sp^2 hybrid orbitals is required.*

sp Hybridization

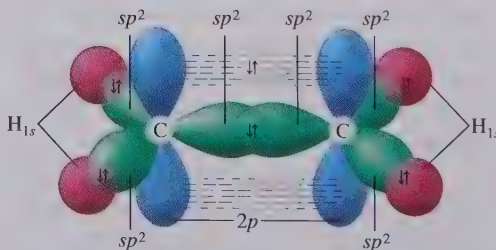
Another type of hybridization occurs in carbon dioxide, which has the following Lewis structure:



In the CO_2 molecule the carbon atom has two effective pairs that will be arranged at an angle of 180 degrees. We therefore need a pair of atomic orbitals oriented in opposite directions. This requires a new type of hybridization, since neither sp^3 nor sp^2 hybrid orbitals will fit this case. To obtain two hybrid orbitals arranged at 180 degrees requires **sp hybridization**, involving one s orbital and one p orbital, as shown in Fig. 9.14.

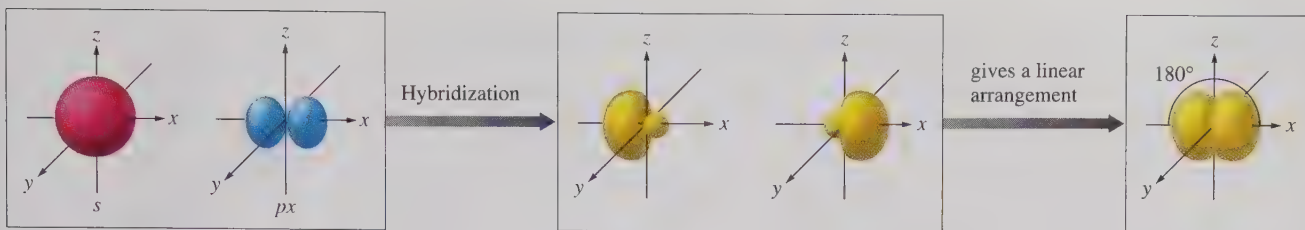
In terms of this model, *two effective pairs around an atom will always require sp hybridization of that atom.* The sp orbitals of carbon in carbon dioxide can be seen in Fig. 9.15, and the corresponding orbital energy-level diagram for their formation is given in Fig. 9.16. These sp hybrid orbitals are used to form the σ bonds between the carbon and the oxygen atoms. Note that two $2p$ orbitals remain unchanged on the sp hybridized carbon. These are used to form the π bonds with the oxygen atoms.

In the CO_2 molecule each oxygen atom* has three effective pairs around it, requiring a trigonal planar arrangement of the pairs. Since a trigonal set of hybrid orbitals requires sp^2 hybridization, each oxygen atom is sp^2 hybridized. One p orbital on each oxygen is unchanged and is used for the π bond with the carbon atom.

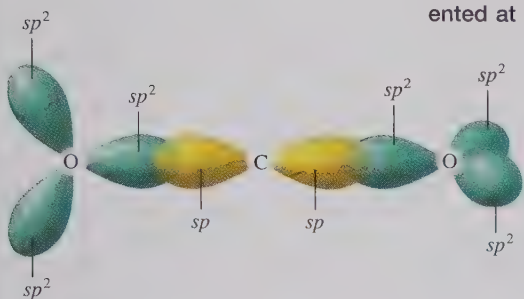


(a)

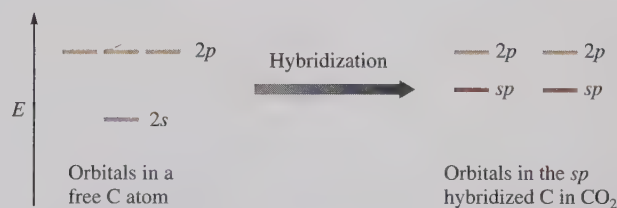
*We will assume that minimizing electron repulsions also is important for the peripheral atoms in a molecule and apply the VSEPR model to these atoms as well.

**FIGURE 9.14**

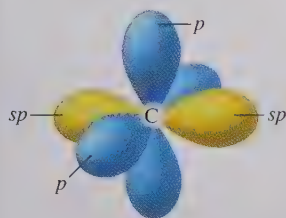
When one s orbital and one p orbital are hybridized, a set of two sp orbitals oriented at 180 degrees results.

**FIGURE 9.15**

The hybrid orbitals in the CO_2 molecule.

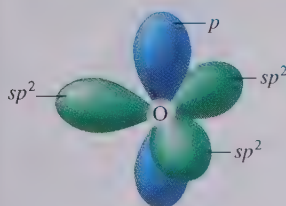
**FIGURE 9.16**

The orbital energy-level diagram for the formation of sp hybrid orbitals on carbon.

**FIGURE 9.17**

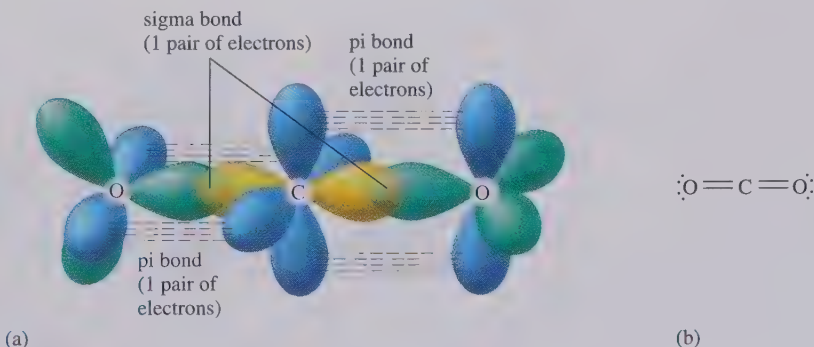
The orbitals of an sp hybridized carbon atom.

More rigorous theoretical models of CO_2 indicate that each of the oxygen atoms uses two p orbitals simultaneously to form the π bonds to the carbon atom, thus leading to unusually strong $\text{C}=\text{O}$ bonds.

**FIGURE 9.18**

The orbital arrangement for an sp^2 hybridized oxygen atom.

Now we are ready to use our model to describe the bonding in carbon dioxide. The sp orbitals on carbon form σ bonds with the sp^2 orbitals on the two oxygen atoms (Fig. 9.15). The remaining sp^2 orbitals on the oxygen atoms hold lone pairs. The π bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel $2p$ orbitals. The sp hybridized carbon atom has two unhybridized p orbitals, pictured in Fig. 9.17. Each of these p orbitals is used to form a π bond with an oxygen atom (see Fig. 9.18). The total bonding picture for the CO_2 molecule is shown in Fig. 9.19. Note that this picture of the bonding neatly explains the arrangement of electrons predicted by the Lewis structure.

**FIGURE 9.19**

(a) The orbitals used to form the bonds in carbon dioxide. Note that the carbon–oxygen double bonds each consist of one σ bond and one π bond.
(b) The Lewis structure for carbon dioxide.

SAMPLE EXERCISE 9.2

The Localized Electron Model II

Describe the bonding in the N_2 molecule.

SOLUTION

The Lewis structure for the nitrogen molecule is



where each nitrogen atom is surrounded by two effective pairs. (Remember that a multiple bond counts as one effective pair.) This gives a linear arrangement (180 degrees) requiring a pair of oppositely directed orbitals. This situation requires sp hybridization. Each nitrogen atom in the nitrogen molecule has two sp hybrid orbitals and two unchanged p orbitals, as shown in Fig. 9.20(a). The sp orbitals are used to form the σ bond between the nitrogen atoms and to hold lone pairs, as shown in Fig. 9.20(b). The p orbitals are used to form the two π bonds [see Fig. 9.20(c)]; each pair of overlapping parallel p orbitals holds one electron pair. Such bonding accounts for the electron arrangement given by the Lewis structure. The triple bond consists of a σ bond (overlap of two sp orbitals) and two π bonds (each one from an overlap of two p orbitals). In addition, a lone pair occupies an sp orbital on each nitrogen atom.

See Exercises 9.13 and 9.14.

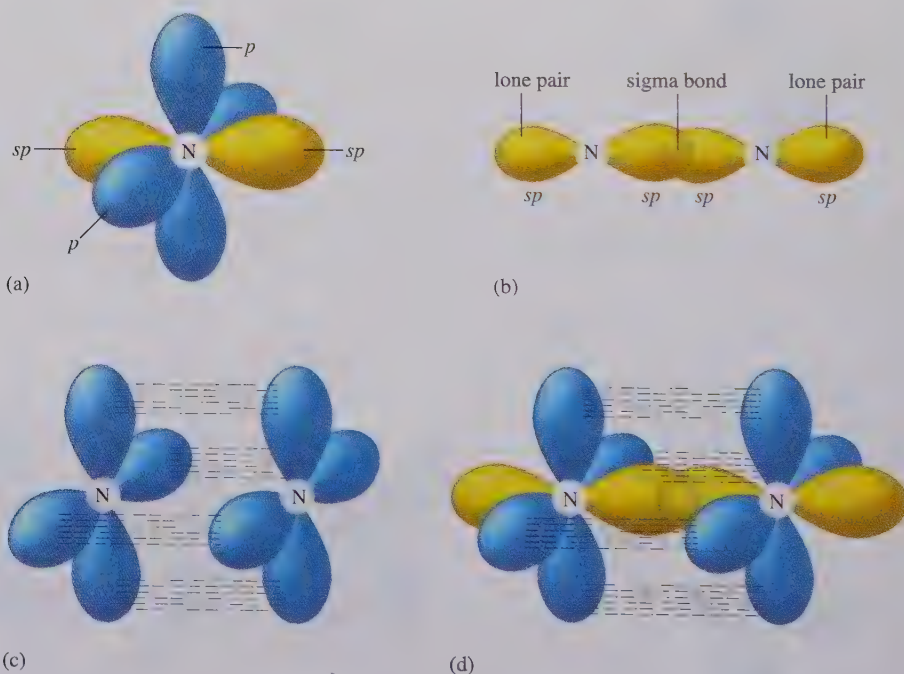
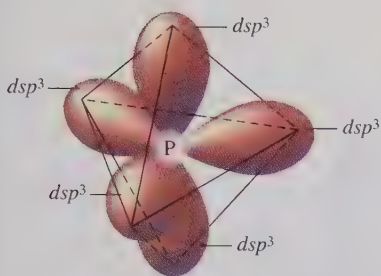


FIGURE 9.20

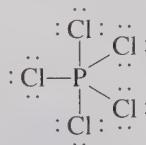
(a) An sp hybridized nitrogen atom. There are two sp hybrid orbitals and two unhybridized p orbitals. (b) The σ bond in the N_2 molecule. (c) The two π bonds in N_2 are formed when electron pairs are shared between two sets of parallel p orbitals. (d) The total bonding picture for N_2 .

**FIGURE 9.21**

A set of dsp^3 hybrid orbitals on a phosphorus atom. Note that the set of five dsp^3 orbitals has a trigonal bipyramidal arrangement. (Each dsp^3 orbital also has a small lobe that is not shown in this diagram.)

dsp^3 Hybridization

To illustrate the treatment of a molecule in which the central atom exceeds the octet rule, consider the bonding in the phosphorus pentachloride molecule (PCl_5). The Lewis structure



shows that the phosphorus atom is surrounded by five electron pairs. Since five pairs require a trigonal bipyramidal arrangement, we need a trigonal bipyramidal set of atomic orbitals on phosphorus. Such a set of orbitals is formed by **dsp^3 hybridization** of one d orbital, one s orbital, and three p orbitals, as shown in Fig. 9.21.

The dsp^3 hybridized phosphorus atom in the PCl_5 molecule uses its five dsp^3 orbitals to share electrons with the five chlorine atoms. *Note that a set of five effective pairs around a given atom always requires a trigonal bipyramidal arrangement, which in turn requires dsp^3 hybridization of that atom.*

The Lewis structure for PCl_5 shows that each chlorine atom is surrounded by four electron pairs. This requires a tetrahedral arrangement, which in turn requires a set of four sp^3 orbitals on each chlorine atom.

Now we can describe the bonding in the PCl_5 molecule. The five $\text{P}-\text{Cl}$ σ bonds are formed by sharing electrons between a dsp^3 orbital* on the phosphorus atom and an sp^3 orbital on each chlorine.[†] The other sp^3 orbitals on each chlorine hold lone pairs. This is shown in Fig. 9.22.

SAMPLE EXERCISE 9.3

The Localized Electron Model III

Describe the bonding in the triiodide ion (I_3^-).

SOLUTION

The Lewis structure for I_3^-



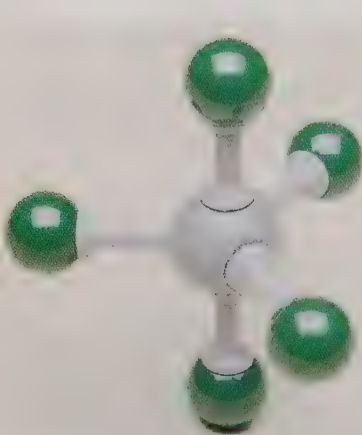
shows that the central iodine atom has five pairs of electrons (see Section 8.11). A set of five pairs requires a trigonal bipyramidal arrangement, which in turn requires a set of dsp^3 orbitals. The outer iodine atoms have four pairs of electrons, which calls for a tetrahedral arrangement and sp^3 hybridization.

Thus the central iodine is dsp^3 hybridized. Three of these hybrid orbitals hold lone pairs, and two of them overlap with sp^3 orbitals of the other two iodine atoms to form σ bonds.

See Exercise 9.21.

* There is considerable controversy about whether the d orbitals are as heavily involved in the bonding in these molecules as this model predicts. However, this matter is beyond the scope of this text.

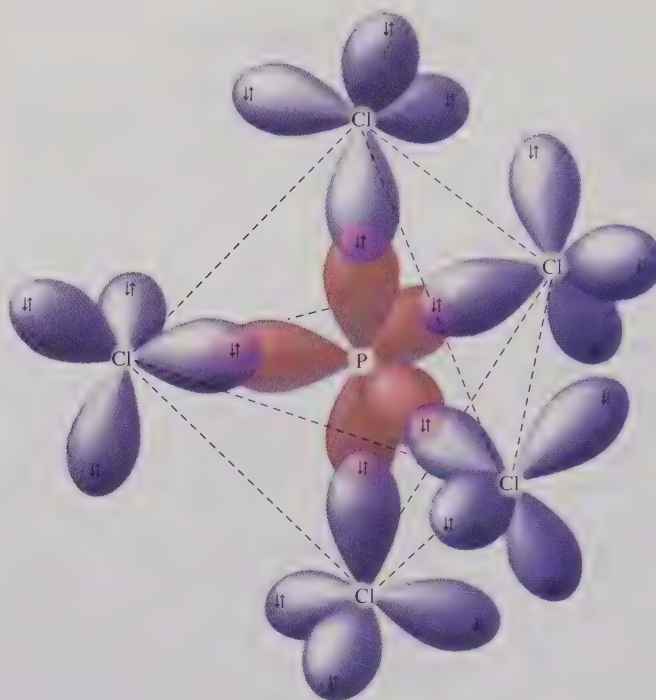
[†] Although we have no way of proving conclusively that each chlorine is sp^3 hybridized, we assume that minimizing electron-pair repulsions is as important for peripheral atoms as for the central atom. Thus we will apply the VSEPR model and hybridization to both central and peripheral atoms.



(a)

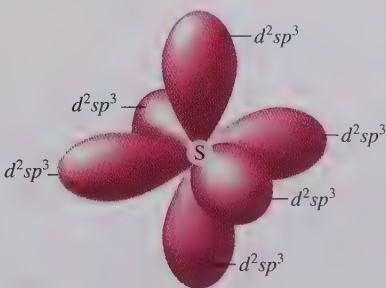
FIGURE 9.22

(a) The structure of the PCl_5 molecule. (b) The orbitals used to form the bonds in PCl_5 . The phosphorus uses a set of five dsp^3 orbitals to share electron pairs with sp^3 orbitals on the five chlorine atoms. The other sp^3 orbitals on each chlorine atom hold lone pairs.



(b)

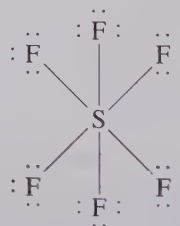
d^2sp^3 hybridization gives six orbitals arranged octahedrally.

**FIGURE 9.23**

An octahedral set of d^2sp^3 orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.

d^2sp^3 Hybridization

Some molecules have six pairs of electrons around a central atom; an example is sulfur hexafluoride (SF_6), which has the Lewis structure



This requires an octahedral arrangement of pairs and in turn an octahedral set of six hybrid orbitals, or d^2sp^3 hybridization, in which two d orbitals, one s orbital, and three p orbitals are combined (see Fig. 9.23). Note that *six electron pairs around an atom are always arranged octahedrally and require d^2sp^3 hybridization of the atom.* Each of the d^2sp^3 orbitals on the sulfur atom is used to bond to a fluorine atom. Since there are four pairs on each fluorine atom, the fluorine atoms are assumed to be sp^3 hybridized.

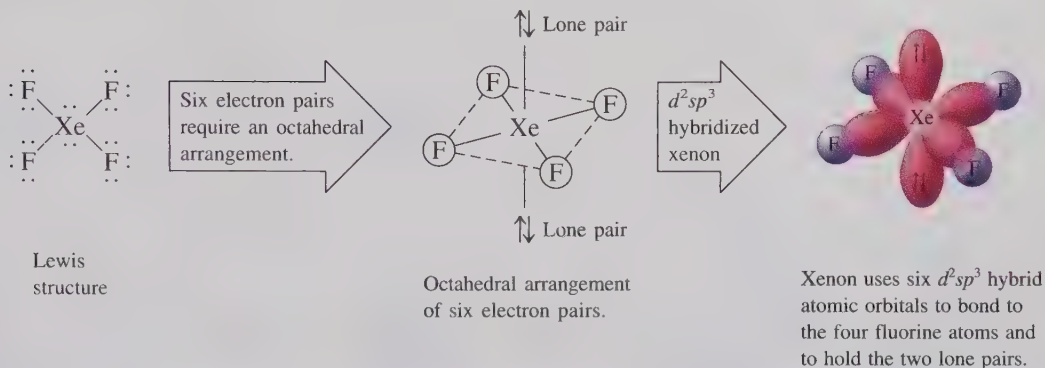
SAMPLE EXERCISE 9.4

The Localized Electron Model IV

How is the xenon atom in XeF_4 hybridized?

SOLUTION

As seen in Sample Exercise 8.13, XeF_4 has six pairs of electrons around xenon that are arranged octahedrally to minimize repulsions. An octahedral set of six atomic orbitals is required to hold these electrons, and the xenon atom is d^2sp^3 hybridized.



See Exercise 9.20.

The Localized Electron Model: A Summary

The description of a molecule using the localized electron model involves three distinct steps.

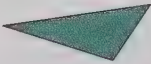
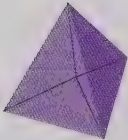
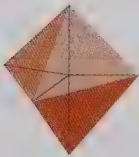
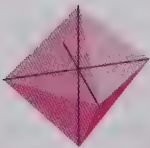
Localized Electron Model

- ➡ **1** Draw the Lewis structure(s).
- ➡ **2** Determine the arrangement of electron pairs using the VSEPR model.
- ➡ **3** Specify the hybrid orbitals needed to accommodate the electron pairs.

It is important to do the steps in this order. For a model to be successful, it must follow nature's priorities. In the case of bonding, it seems clear that the tendency for a molecule to minimize its energy is more important than the maintenance of the characteristics of atoms as they exist in the free state. The atoms adjust to meet the "needs" of the molecule. When considering the bonding in a particular molecule, therefore, we always start with the molecule rather than the component atoms. In the molecule the electrons will be arranged to give each atom a noble gas configuration, where possible, and to minimize electron-pair repulsions. We then assume that the atoms adjust their orbitals by hybridization to allow the molecule to adopt the structure that gives the minimum energy.

In applying the localized electron model, we must remember not to overemphasize the characteristics of the separate atoms. It is not where the valence electrons originate that is important; it is where they are needed in the molecule to achieve stability. In the same vein, it is not the orbitals in the isolated atom that matter, but what orbitals the molecule requires for minimum energy.

The requirements for the various types of hybridization are summarized in Fig. 9.24 on the following page.

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required	
2		Linear	sp
3		Trigonal planar	sp^2
4		Tetrahedral	sp^3
5		Trigonal bipyramidal	dsp^3
6		Octahedral	d^2sp^3

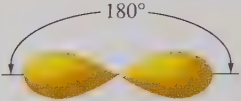
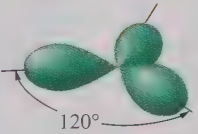
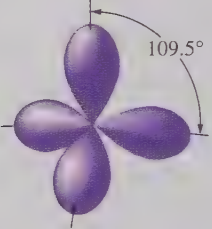
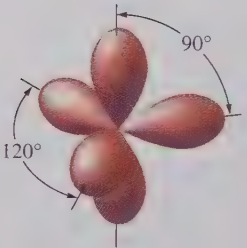
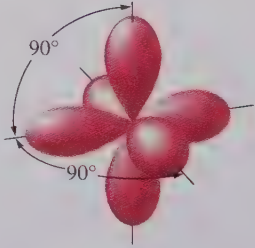






FIGURE 9.24

The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.

SAMPLE EXERCISE 9.5

The Localized Electron Model V

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure.

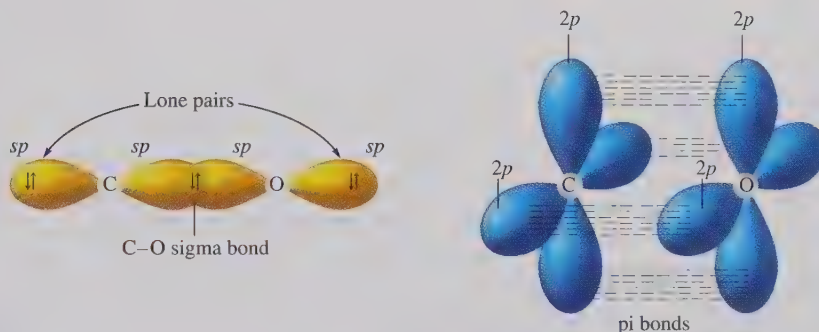
- CO
- BF_4^-
- XeF_2

SOLUTION

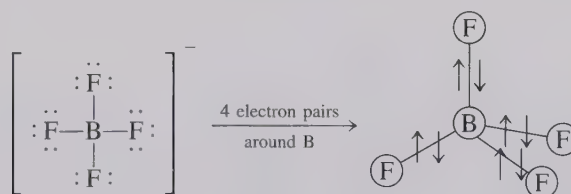
- a. The CO molecule has 10 valence electrons, and its Lewis structure is



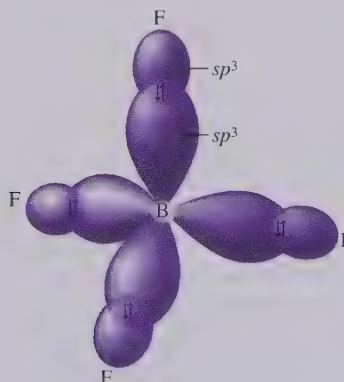
Each atom has two effective pairs, which means that both are sp hybridized. The triple bond consists of a σ bond produced by overlap of an sp orbital from each atom and two π bonds produced by overlap of $2p$ orbitals from each atom. The lone pairs are in sp orbitals. Since the CO molecule has only two atoms, it must be linear.



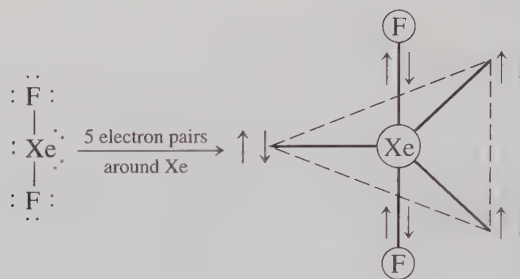
- b. The BF_4^- ion has 32 valence electrons. The Lewis structure shows four pairs of electrons around the boron atom, which means a tetrahedral arrangement:



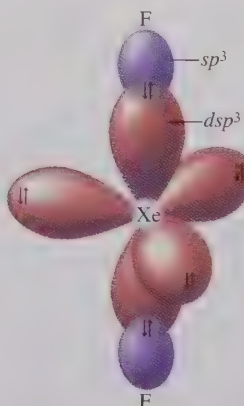
This requires sp^3 hybridization of the boron atom. Each fluorine atom also has four electron pairs and can be assumed to be sp^3 hybridized (only one sp^3 orbital is shown for each fluorine atom). The BF_4^- ion's molecular structure is tetrahedral.



- c. The XeF_2 molecule has 22 valence electrons. The Lewis structure shows five electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:



Note that the lone pairs are placed in the plane where they are 120 degrees apart. To accommodate five pairs at the vertices of a trigonal bipyramid requires that the xenon atom adopt a set of five dsp^3 orbitals. Each fluorine atom has four electron pairs and can be assumed to be sp^3 hybridized. The XeF_2 molecule has a linear arrangement of atoms.



See Exercises 9.21 and 9.22.

9.2 The Molecular Orbital Model

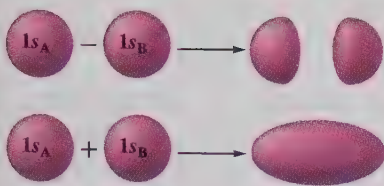


Understanding Concepts: Molecular Orbitals in H_2

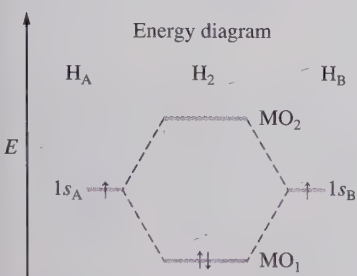
Molecular orbital theory parallels the atomic theory discussed in Chapter 7.

We have seen that the localized electron model is of great value in interpreting the structure and bonding of molecules. However, there are some problems with this model. For example, it incorrectly assumes that electrons are localized, and so the concept of resonance must be added. Also, the model does not deal effectively with molecules containing unpaired electrons. And finally, the model gives no direct information about bond energies.

Another model often used to describe bonding is the **molecular orbital model**. To introduce the assumptions, methods, and results of this model, we will consider the simplest of all molecules, H_2 , which consists of two protons and two electrons. A very stable molecule, H_2 is lower in energy than the separated hydrogen atoms by 432 kJ/mol.

**FIGURE 9.25**

The combination of hydrogen 1s atomic orbitals to form molecular orbitals.



(a)

Electron probability distribution



(b)

FIGURE 9.26

(a) The molecular orbital energy-level diagram for the H_2 molecule.
(b) The shapes of the molecular orbitals are obtained by squaring the wave functions for MO_1 and MO_2 .

Since the hydrogen molecule consists of protons and electrons, the same components found in separated hydrogen atoms, it seems reasonable to use a theory similar to the atomic theory discussed in Chapter 7, which assumes that the electrons in an atom exist in orbitals of a given energy. Can we apply this same type of model to the hydrogen molecule? Yes. In fact, describing the H_2 molecule in terms of quantum mechanics is quite straightforward.

However, even though it is formulated rather easily, this problem cannot be solved exactly. The difficulty is the same as that in dealing with polyelectronic atoms—the electron correlation problem. Since we do not know the details of the electron movements, we cannot deal with the electron–electron interactions in a specific way. We need to make approximations that allow a solution of the problem but do not destroy the model’s physical integrity. The success of these approximations can only be measured by comparing predictions based on theory with experimental observations. In this case we will see that the simplified model works very well.

Just as atomic orbitals are solutions to the quantum mechanical treatment of atoms, **molecular orbitals (MOs)** are solutions to the molecular problem. Molecular orbitals have many of the same characteristics as atomic orbitals. Two of the most important are that they can hold two electrons with opposite spins and that the square of the molecular orbital wave function indicates electron probability.

We will now describe the bonding in the hydrogen molecule using this model. The first step is to obtain the hydrogen molecule’s orbitals, a process that is greatly simplified if we assume that the molecular orbitals can be constructed from the hydrogen 1s atomic orbitals.

When the quantum mechanical equations for the hydrogen molecule are solved, two molecular orbitals result, which can be represented as

$$\begin{aligned}\text{MO}_1 &= 1s_A + 1s_B \\ \text{MO}_2 &= 1s_A - 1s_B\end{aligned}$$

where $1s_A$ and $1s_B$ represent the 1s orbitals from the two separated hydrogen atoms. This process is shown schematically in Fig. 9.25.

The orbital properties of most interest are size, shape (described by the electron probability distribution), and energy. These properties for the hydrogen molecular orbitals are represented in Fig. 9.26. From Fig. 9.26 we can note several important points:

1. The electron probability of both molecular orbitals is centered along the line passing through the two nuclei. For MO_1 the greatest electron probability is *between* the nuclei, and for MO_2 it is on *either side* of the nuclei. This type of electron distribution is described as *sigma* (σ), as in the localized electron model. Accordingly, we refer to MO_1 and MO_2 as **sigma (σ) molecular orbitals**.
2. In the molecule only the molecular orbitals are available for occupation by electrons. The 1s atomic orbitals of the hydrogen atoms no longer exist, because the H_2 molecule—a new entity—has its own set of new orbitals.
3. MO_1 is lower in energy than the 1s orbitals of free hydrogen atoms, while MO_2 is higher in energy than the 1s orbitals. This fact has very important implications for the stability of the H_2 molecule, since if the two electrons (one from each hydrogen atom) occupy the lower-energy MO_1 , they will have lower energy than they do in the two separate hydrogen atoms. This situation favors molecule formation, because nature tends to seek the lowest energy state. That is, the driving force for molecule formation is that the molecular orbital available

Visualization: Sigma orbitals and Bonding and Antibonding

Bonding will result if the molecule has lower energy than the separated atoms.

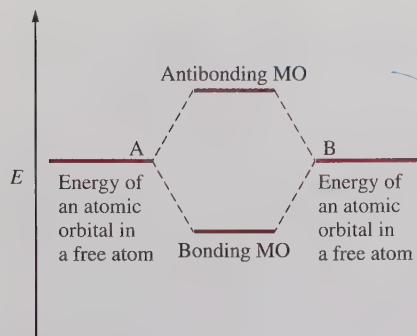


FIGURE 9.27
Bonding and antibonding molecular orbitals (MOs).

to the two electrons has lower energy than the atomic orbitals these electrons occupy in the separated atoms. This situation is favorable to bonding, or *probonding*.

On the other hand, if the two electrons were forced to occupy the higher-energy MO_2 , they would be definitely *antibonding*. In this case, these electrons would have lower energy in the separated atoms than in the molecule, and the separated state would be favored. Of course, since the lower-energy MO_1 is available, the two electrons occupy that MO and the molecule is stable.

We have seen that the molecular orbitals of the hydrogen molecule fall into two classes: bonding and antibonding. A **bonding molecular orbital** is *lower in energy than the atomic orbitals of which it is composed*. Electrons in this type of orbital will favor the molecule; that is, they will favor bonding. An **antibonding molecular orbital** is *higher in energy than the atomic orbitals of which it is composed*. Electrons in this type of orbital will favor the separated atoms (they are antibonding). Figure 9.27 illustrates these ideas.

- Figure 9.26 shows that for the bonding molecular orbital in the H_2 molecule the electrons have the greatest probability of being between the nuclei. This is exactly what we would expect, since the electrons can lower their energies by being simultaneously attracted by both nuclei. On the other hand, the electron distribution for the antibonding molecular orbital is such that the electrons are mainly outside the space between the nuclei. This type of distribution is not expected to provide any bonding force. In fact, it causes the electrons to be higher in energy than in the separated atoms. Thus the molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding. This fact reassures us that the model is physically reasonable.
- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding. Antibonding character is indicated by an asterisk. For the H_2 molecule, both MOs have σ symmetry, and both are constructed from hydrogen $1s$ atomic orbitals. The molecular orbitals for H_2 are therefore labeled as follows:

$$MO_1 = \sigma_{1s}$$

$$MO_2 = \sigma_{1s}^*$$

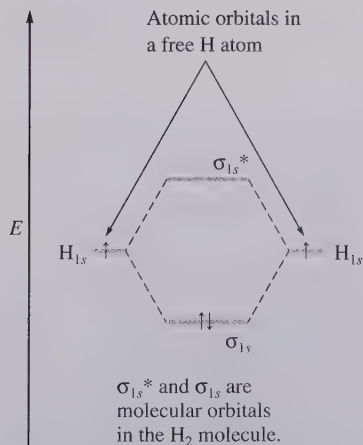


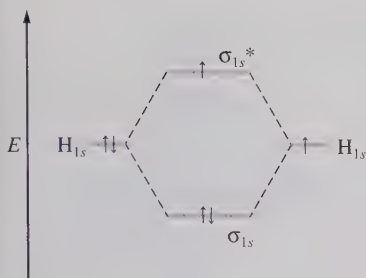
FIGURE 9.28
A molecular orbital energy-level diagram for the H_2 molecule.

- Molecular electron configurations can be written in much the same way as atomic (electron) configurations. Since the H_2 molecule has two electrons in the σ_{1s} molecular orbital, the electron configuration is σ_{1s}^2 .
- Each molecular orbital can hold two electrons, but the spins must be opposite.
- Orbitals are conserved. The number of molecular orbitals will always be the same as the number of atomic orbitals used to construct them.

Many of the above points are summarized in Fig. 9.28.

Now suppose we could form the H_2^- ion from a hydride ion (H^-) and a hydrogen atom. Would this species be stable? Since the H^- ion has the configuration $1s^2$ and the H atom has a $1s^1$ configuration, we will use $1s$ atomic orbitals to construct the MO diagram for the H_2^- ion, as shown in Fig. 9.29. The electron configuration for H_2^- is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$.

The key idea is that the H_2^- ion will be stable if it has a lower energy than its separated parts. From Fig. 9.29 we see that in going from the separated H^- ion and

**FIGURE 9.29**

The molecular orbital energy-level diagram for the H_2^- ion.

Although the model predicts that H_2^- should be stable, this ion has never been observed, again emphasizing the perils of simple models.

H atom to the H_2^- ion, the model predicts that two electrons are lowered in energy and one electron is raised in energy. In other words, two electrons are bonding and one electron is antibonding. Since more electrons favor bonding, H_2^- is predicted to be a stable entity—a bond has formed. But how would we expect the bond strengths in the molecules of H_2 and H_2^- to compare?

In the formation of the H_2 molecule, two electrons are lowered in energy and no electrons are raised in energy compared with the parent atoms. When H_2^- is formed, two electrons are lowered in energy and one is raised, producing a *net lowering of the energy of only one electron*. Thus the model predicts that H_2 is *twice as stable* as H_2^- with respect to their separated components. In other words, the bond in the H_2 molecule is predicted to be about twice as strong as the bond in the H_2^- ion.

Bond Order

To indicate bond strength, we use the concept of bond order. **Bond order** is the *difference between the number of bonding electrons and the number of antibonding electrons divided by two*.

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

We divide by 2 because, from the localized electron model, we are used to thinking of bonds in terms of *pairs* of electrons.

Since the H_2 molecule has two bonding electrons and no antibonding electrons, the bond order is

$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

The H_2^- ion has two bonding electrons and one antibonding electron; the bond order is

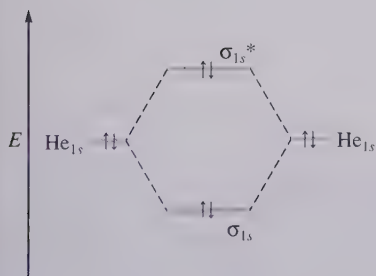
$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2}$$

Bond order is an indication of bond strength because it reflects the difference between the number of bonding electrons and the number of antibonding electrons. *Larger bond order means greater bond strength.*

We will now apply the molecular orbital model to the helium molecule (He_2). Does this model predict that this molecule will be stable? Since the He atom has a $1s^2$ configuration, $1s$ orbitals are used to construct the molecular orbitals, and the molecule will have four electrons. From the diagram shown in Fig. 9.30 it is apparent that two electrons are raised in energy and two are lowered in energy. Thus the bond order is zero:

$$\frac{2 - 2}{2} = 0$$

This implies that the He_2 molecule is *not* stable with respect to the two free He atoms, which agrees with the observation that helium gas consists of individual He atoms.

**FIGURE 9.30**

The molecular orbital energy-level diagram for the He_2 molecule.

9.3 Bonding in Homonuclear Diatomic Molecules

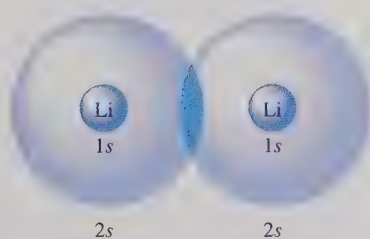


FIGURE 9.31

The relative sizes of the lithium 1s and 2s atomic orbitals.

In this section we consider *homonuclear diatomic molecules* (those composed of two identical atoms) of elements in Period 2 of the periodic table. Since the lithium atom has a $1s^2 2s^1$ electron configuration, it would seem that we should use the Li 1s and 2s orbitals to form the molecular orbitals of the Li_2 molecule. However, the 1s orbitals on the lithium atoms are much smaller than the 2s orbitals and therefore do not overlap in space to any appreciable extent (see Fig. 9.31). Thus the two electrons in each 1s orbital can be assumed to be localized and not to participate in the bonding. *To participate in molecular orbitals, atomic orbitals must overlap in space.* This means that only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.

The molecular orbital diagram of the Li_2 molecule and the shapes of its bonding and antibonding MOs are shown in Fig. 9.32. The electron configuration for Li_2 (valence electrons only) is σ_{2s}^2 , and the bond order is

$$\frac{2 - 0}{2} = 1$$

The Li_2 is a stable molecule (has lower energy than two separated lithium atoms). However, this does not mean that Li_2 is the most stable form of elemental lithium. In fact, at normal temperature and pressure, lithium exists as a solid containing many lithium atoms bound to each other.

For the beryllium molecule (Be_2) the bonding and antibonding orbitals both contain two electrons. In this case the bond order is $(2 - 2)/2 = 0$, and since Be_2 is not more stable than two separated Be atoms, no molecule forms. However, beryllium metal contains many beryllium atoms bonded to each other and is stable for reasons we will discuss in Chapter 10.

Since the boron atom has a $1s^2 2s^2 2p^1$ configuration, we describe the B_2 molecule by considering how p atomic orbitals combine to form molecular orbitals. Recall that p orbitals have two lobes and that they occur in sets of three mutually perpendicular orbitals [see Fig. 9.33(a)]. When two B atoms approach each other, two pairs of p orbitals can overlap in a parallel fashion [Fig. 9.33(b) and (c)] and one pair can overlap head-on [Fig. 9.33(d)].

First, let's consider the molecular orbitals from the head-on overlap, as shown in Fig. 9.34(a). Note that the electrons in the bonding MO are, as expected, concentrated between the nuclei, and the electrons in the antibonding MO are concentrated outside the area between the two nuclei. Also, both these MOs are σ molecular orbitals. The p orbitals that overlap in a parallel fashion also produce bonding and antibonding orbitals [Fig. 9.34(b)]. Since the electron probability lies above and



Beryllium metal.

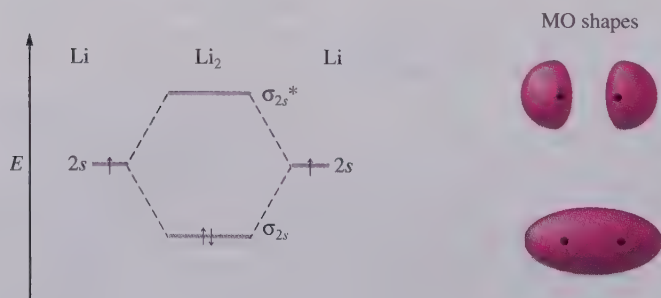
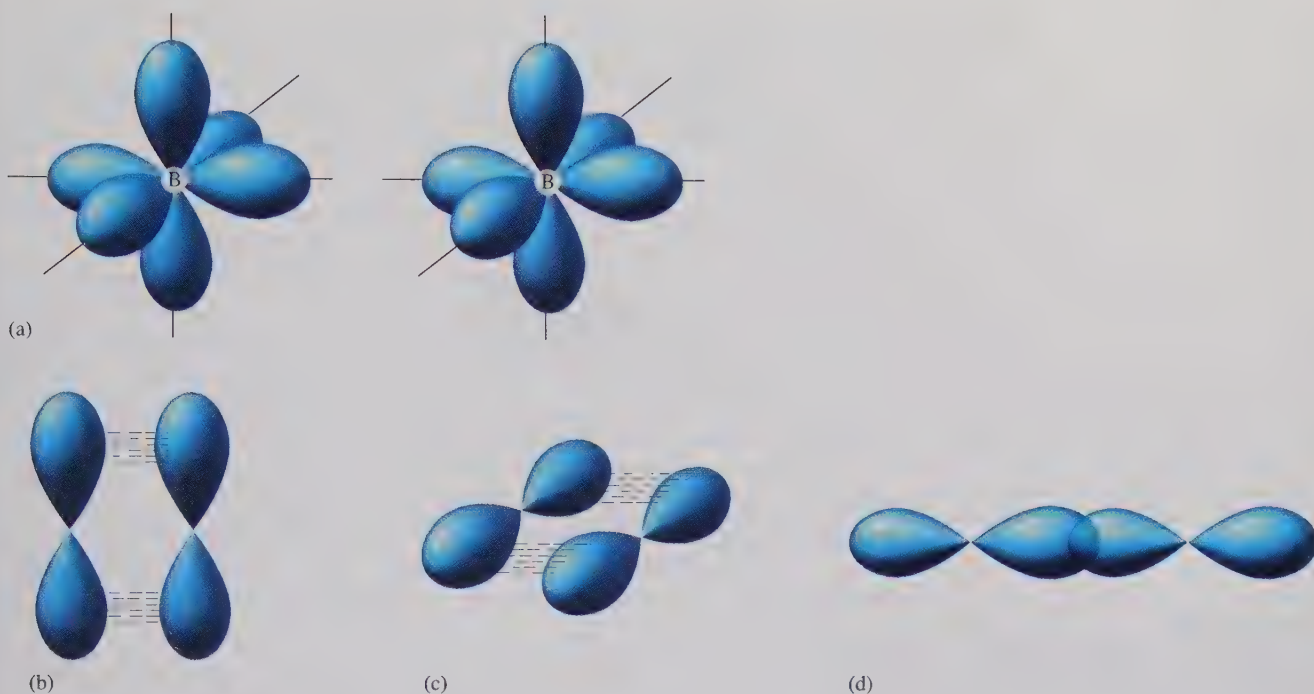
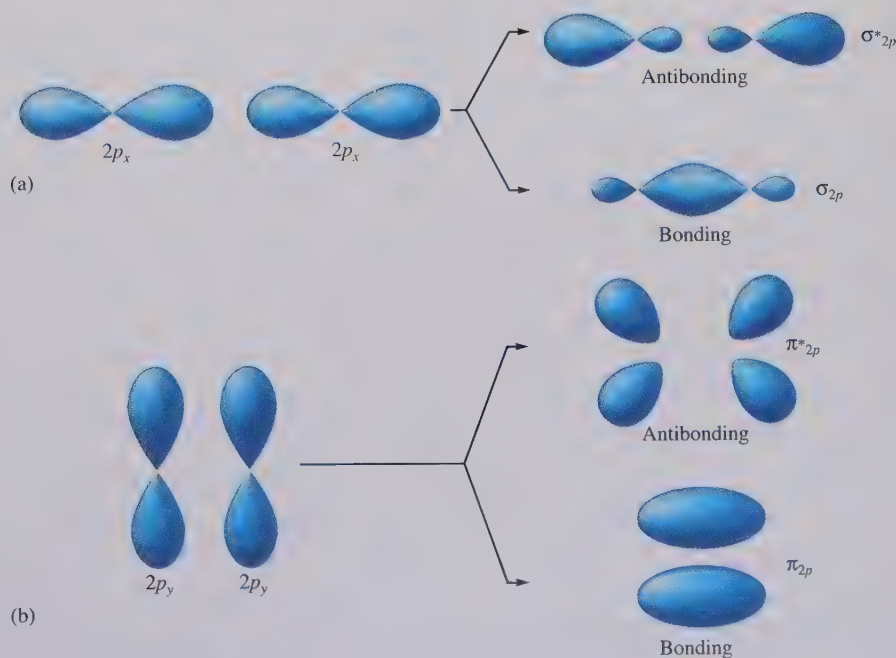


FIGURE 9.32

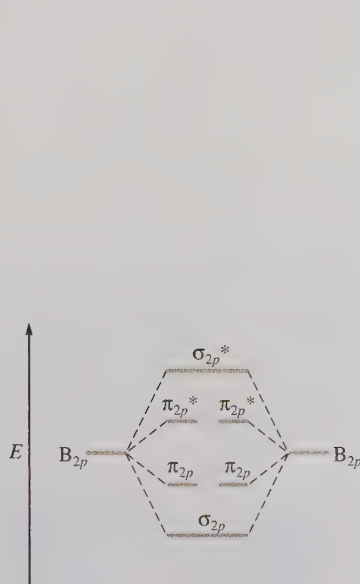
The molecular orbital energy-level diagram for the Li_2 molecule.

**FIGURE 9.33**

(a) The three mutually perpendicular $2p$ orbitals on two adjacent boron atoms. Two pairs of parallel p orbitals can overlap as shown in (b) and (c), and the third pair can overlap head-on as shown in (d).

**FIGURE 9.34**

(a) The two p orbitals on the boron atom that overlap head-on produce two σ molecular orbitals, one bonding and one antibonding. (b) Two p orbitals that lie parallel overlap to produce two π molecular orbitals, one bonding and one antibonding.

**FIGURE 9.35**

The *expected* molecular orbital energy-level diagram resulting from the combination of the $2p$ orbitals on two boron atoms.

below the line between the nuclei, both the orbitals are **pi (π) molecular orbitals**. They are designated as π_{2p} for the bonding MO and π_{2p}^* for the antibonding MO.

Let's try to make an educated guess about the relative energies of the σ and π molecular orbitals formed from the $2p$ atomic orbitals. Would we expect the electrons to prefer the σ bonding orbital (where the electron probability is concentrated in the area between the nuclei) or the π bonding orbital? The σ orbital would seem to have the lower energy, since the electrons are closest to the two nuclei. This agrees with the observation that σ interactions are stronger than π interactions.

Figure 9.35 gives the molecular orbital energy-level diagram *expected* when the two sets of $2p$ orbitals on the boron atoms combine to form molecular orbitals. Note that there are two π bonding orbitals at the same energy (degenerate orbitals) formed from the two pairs of parallel p orbitals, and there are two degenerate π antibonding orbitals. The energy of the π_{2p} orbitals is expected to be higher than that of the σ_{2p} orbital because σ interactions are generally stronger than π interactions.

To construct the total molecular orbital diagram for the B_2 molecule, we make the assumption that the $2s$ and $2p$ orbitals combine separately (in other words, there is no $2s$ – $2p$ mixing). The resulting diagram is shown in Fig. 9.36. Note that B_2 has six *valence* electrons. (Remember the $1s$ orbitals and electrons are assumed not to participate in the bonding.) This diagram predicts the bond order:

$$\frac{4 - 2}{2} = 1$$

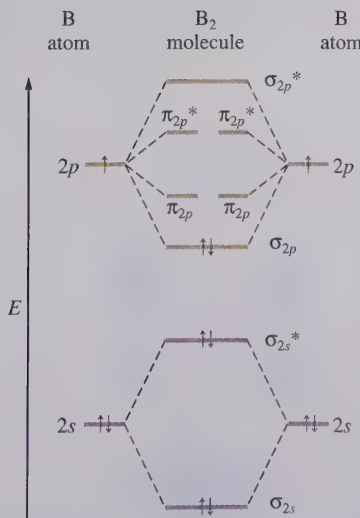
Therefore, B_2 should be a stable molecule.

Paramagnetism

At this point we need to discuss an additional molecular property—magnetism. Most materials have no magnetism until they are placed in a magnetic field. However, in the presence of such a field, magnetism of two types can be induced. **Paramagnetism** causes the substance to be attracted into the inducing magnetic field. **Diamagnetism** causes the substance to be repelled from the inducing magnetic field. Figure 9.37 illustrates how paramagnetism is measured. The sample is weighed with the electromagnet turned off and then weighed again with the electromagnet turned on. An increase in weight when the field is turned on indicates the sample is paramagnetic. Studies have shown that *paramagnetism is associated with unpaired electrons and diamagnetism is associated with paired electrons*. Any substance that has both paired and unpaired electrons will exhibit a net paramagnetism, since the effect of paramagnetism is much stronger than that of diamagnetism.

The molecular orbital energy-level diagram represented in Fig. 9.36 predicts that the B_2 molecule will be diamagnetic, since the MOs contain only paired electrons. However, experiments show that B_2 is actually paramagnetic with two unpaired electrons. Why does the model yield the wrong prediction? This is yet another illustration of how models are developed and used. In general, we try to use the simplest possible model that accounts for all the important observations. In this case, although the simplest model successfully describes the diatomic molecules up to B_2 , it certainly is suspect if it cannot describe the B_2 molecule correctly. This means we must either discard the model or find a way to modify it.

Let's consider one assumption that we made. In our treatment of B_2 , we have assumed that the s and p orbitals combine separately to form molecular orbitals. Calculations show that when the s and p orbitals are allowed to mix in the same molecular orbital, a different energy-level diagram results for B_2 (see Fig. 9.38).

**FIGURE 9.36**

The *expected* molecular orbital energy-level diagram for the B_2 molecule.

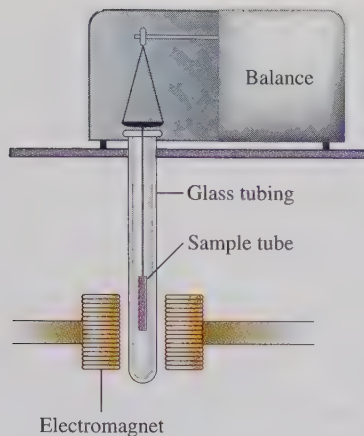
**FIGURE 9.37**

Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.

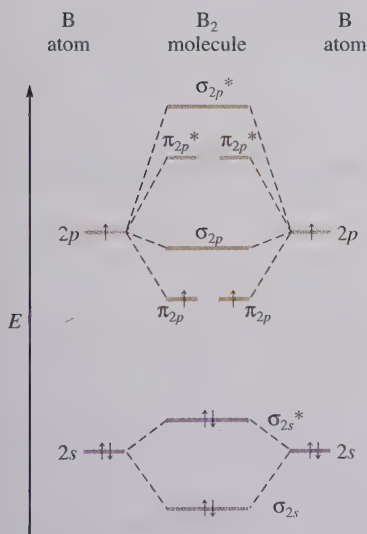
Note that even though the s and p contributions to the MOs are no longer separate, we retain the simple orbital designations. The energies of π_{2p} and σ_{2p} orbitals are reversed by p - s mixing, and the σ_{2s} and the σ_{2s}^* orbitals are no longer equally spaced relative to the energy of the free $2s$ orbital.

When the six valence electrons for the B_2 molecule are placed in the modified energy-level diagram, each of the last two electrons goes into one of the degenerate π_{2p} orbitals. This produces a paramagnetic molecule in agreement with experimental results. Thus, when the model is extended to allow p - s mixing in molecular orbitals, it predicts the correct magnetism. Note that the bond order is $(4 - 2)/2 = 1$, as before.

The remaining diatomic molecules of the elements in Period 2 can be described using similar ideas. For example, the C_2 and N_2 molecules use the same set of orbitals as for B_2 (see Fig. 9.38). Because the importance of $2s$ - $2p$ mixing decreases across the period, the σ_{2p} and π_{2p} orbitals revert to the order expected in the absence of $2s$ - $2p$ mixing for the molecules O_2 and F_2 , as shown in Fig. 9.39.

Several significant points arise from the orbital diagrams, bond strengths, and bond lengths summarized in Fig. 9.39 for the Period 2 diatomics:

1. There are definite correlations between bond order, bond energy, and bond length. As the bond order predicted by the molecular orbital model increases, the bond energy increases and the bond length decreases. This is a clear indication that the bond order predicted by the model accurately reflects bond strength, and it strongly supports the reasonableness of the MO model.
2. Comparison of the bond energies of the B_2 and F_2 molecules indicates that bond order cannot automatically be associated with a particular bond energy. Although both molecules have a bond order of 1, the bond in B_2 appears to be about twice as strong as the bond in F_2 . As we will see in our later discussion of the halogens, F_2 has an unusually weak single bond due to larger than usual electron-electron repulsions (there are 14 valence electrons on the small F_2 molecule).
3. Note the very large bond energy associated with the N_2 molecule, which the molecular orbital model predicts will have a bond order of 3, a triple bond. The very strong bond in N_2 is the principal reason that many nitrogen-containing

**FIGURE 9.38**

The *correct* molecular orbital energy-level diagram for the B_2 molecule. When p - s mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed. The two electrons from the B $2p$ orbitals now occupy separate, degenerate π_{2p} molecular orbitals and thus have parallel spins. Therefore, this diagram explains the observed paramagnetism of B_2 .

	B ₂	C ₂	N ₂	O ₂	F ₂
σ_{2p}^*	—	—	—	σ_{2p}^* —	—
π_{2p}^*	—	—	—	π_{2p}^* $\uparrow$ $\uparrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}	—	—	$\uparrow\downarrow$	π_{2p} $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
π_{2p}	$\uparrow$ $\uparrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	σ_{2p} $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s}^* $\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ_{2s} $\uparrow\downarrow$	$\uparrow\downarrow$
Magnetism	Para-magnetic	Dia-magnetic	Dia-magnetic	Para-magnetic	Dia-magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

FIGURE 9.39

The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic molecules B₂ through F₂. Note that for O₂ and F₂ the σ_{2p} orbital is lower in energy than the π_{2p} orbitals.



Visualization: Magnetic Properties of Liquid Nitrogen and Oxygen

compounds are used as high explosives. The reactions involving these explosives give the very stable N₂ molecule as a product, thus releasing large quantities of energy.

- The O₂ molecule is known to be paramagnetic. This can be very convincingly demonstrated by pouring liquid oxygen between the poles of a strong magnet, as shown in Fig. 9.40. The oxygen remains there until it evaporates. Significantly, the molecular orbital model correctly predicts oxygen's paramagnetism, while the localized electron model predicts a diamagnetic molecule.

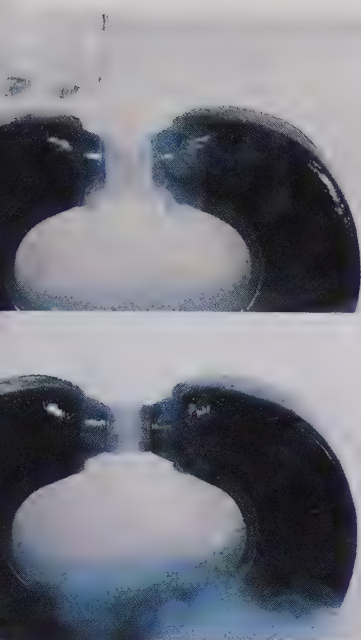
SAMPLE EXERCISE 9.6

The Molecular Orbital Model I

For the species O₂, O₂⁺, and O₂[−], give the electron configuration and the bond order for each. Which has the strongest bond?

SOLUTION

The O₂ molecule has 12 valence electrons (6 + 6); O₂⁺ has 11 valence electrons (6 + 6 − 1); and O₂[−] has 13 valence electrons (6 + 6 + 1). We will assume that

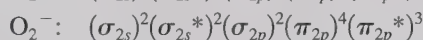
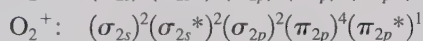
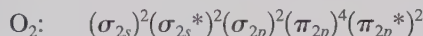
**FIGURE 9.40**

When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the O_2 molecule.

the ions can be treated using the same molecular orbital diagram as for the neutral diatomic molecule:

	O_2	O_2^+	O_2^-
σ_{2p}^*	—	—	—
π_{2p}^*	$\uparrow \uparrow$	$\uparrow$ —	$\uparrow\downarrow \uparrow$
π_{2p}	$\uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow$
σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

The electron configuration for each species can then be taken from the diagram:



The bond orders are:

$$\text{For } O_2: \frac{8 - 4}{2} = 2$$

$$\text{For } O_2^+: \frac{8 - 3}{2} = 2.5$$

$$\text{For } O_2^-: \frac{8 - 5}{2} = 1.5$$

Thus O_2^+ is expected to have the strongest bond of the three species.

See Exercises 9.35 through 9.36.

SAMPLE EXERCISE 9.7

The Molecular Orbital Model II

Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules.

- Ne_2
- P_2

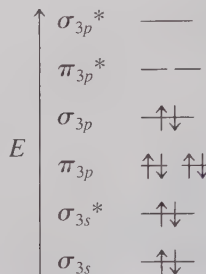
SOLUTION

- The valence orbitals for Ne are $2s$ and $2p$. Thus we can use the molecular orbitals we have already constructed for the diatomic molecules of the Period 2 elements. The Ne_2 molecule has 16 valence electrons (8 from each atom). Placing these electrons in the appropriate molecular orbitals produces the following diagram:

E	$\uparrow$	σ_{2p}^*	$\uparrow\downarrow$
		π_{2p}^*	$\uparrow\downarrow \uparrow\downarrow$
		π_{2p}	$\uparrow\downarrow \uparrow\downarrow$
		σ_{2p}	$\uparrow\downarrow$
		σ_{2s}^*	$\uparrow\downarrow$
		σ_{2s}	$\uparrow\downarrow$

The bond order is $(8 - 8)/2 = 0$, and Ne_2 does not exist.

- b. The P_2 molecule contains phosphorus atoms from the third row of the periodic table. We will assume that the diatomic molecules of the Period 3 elements can be treated in a way very similar to that which we have used so far. Thus we will draw the MO diagram for P_2 analogous to that for N_2 . The only change will be that the molecular orbitals will be formed from $3s$ and $3p$ atomic orbitals. The P_2 model has 10 valence electrons (5 from each phosphorus atom). The resulting molecular orbital diagram is



The molecule has a bond order of 3 and is expected to be diamagnetic.

See Exercises 9.33 and 9.36.

9.4 Bonding in Heteronuclear Diatomic Molecules

In this section we will deal with selected examples of **heteronuclear** (different atoms) **diatomic molecules**. A special case involves molecules containing atoms adjacent to each other in the periodic table. Since the atoms involved in such a molecule are so similar, we can use the molecular orbital diagram for homonuclear molecules. For example, we can predict the bond order and magnetism of nitric oxide (NO) by placing its 11 valence electrons (5 from nitrogen and 6 from oxygen) in the molecular orbital energy-level diagram shown in Fig. 9.41. The molecule should be paramagnetic and has a bond order of

$$\frac{8 - 3}{2} = 2.5$$

Experimentally, nitric oxide is indeed found to be paramagnetic. Notice that this odd-electron molecule is described very naturally by the MO model. In contrast, the localized electron model, in the simple form used in this text, cannot be used readily to treat such molecules.

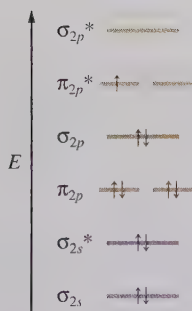


FIGURE 9.41

The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for N_2 . The bond order is 2.5.

SAMPLE EXERCISE 9.8

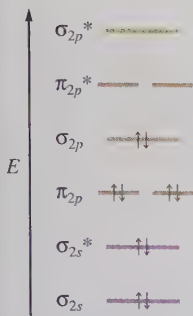
The Molecular Orbital Model III

Use the molecular orbital model to predict the magnetism and bond order of the NO^+ and CN^- ions.

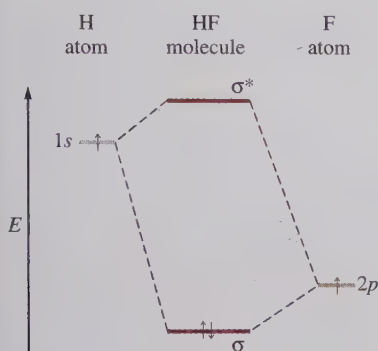
SOLUTION

The NO^+ ion has 10 valence electrons ($5 + 6 - 1$). The CN^- ion also has 10 valence electrons ($4 + 5 + 1$). Both ions are therefore diamagnetic and have a bond order derived from the equation

$$\frac{8 - 2}{2} = 3$$

**FIGURE 9.42**

The molecular orbital energy-level diagram for both the NO^+ and CN^- ions.

**FIGURE 9.43**

A partial molecular orbital energy-level diagram for the HF molecule.

The molecular orbital diagram for these two ions is the same (see Fig. 9.42).

See Exercises 9.37 and 9.38.

When the two atoms of a diatomic molecule are very different, the energy-level diagram for homonuclear molecules can no longer be used. A new diagram must be devised for each molecule. We will illustrate this case by considering the hydrogen fluoride (HF) molecule. The electron configurations of the hydrogen and fluorine atoms are $1s^1$ and $1s^2 2s^2 2p^5$, respectively. To keep things as simple as possible, we will assume that fluorine uses only one of its $2p$ orbitals to bond to hydrogen. Thus the molecular orbitals for HF will be composed of fluorine $2p$ and hydrogen $1s$ orbitals. Figure 9.43 gives the partial molecular orbital energy-level diagram for HF, focusing only on the orbitals involved in the bonding. We are assuming that fluorine's other valence electrons remain localized on the fluorine. The $2p$ orbital of fluorine is shown at a lower energy than the $1s$ orbital of hydrogen on the diagram because fluorine binds its valence electrons more tightly. Thus the $2p$ electron on a free fluorine atom is at lower energy than the $1s$ electron on a free hydrogen atom. The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.

Because the fluorine $2p$ orbital is lower in energy than the hydrogen $1s$ orbital, the electrons prefer to be closer to the fluorine atom. That is, the σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine (see Fig. 9.44). The electron pair is not shared equally. This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive. This is *exactly* the bond polarity observed for HF. Thus the molecular orbital model accounts in a straightforward way for the different electronegativities of hydrogen and fluorine and the resulting unequal charge distribution.

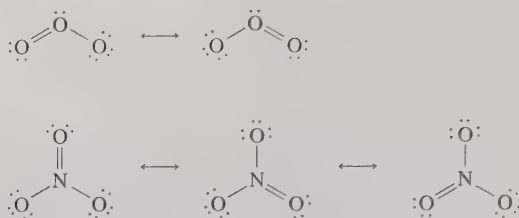
9.5 Combining the Localized Electron and Molecular Orbital Models

One of the main difficulties with the localized electron model is its assumption that electrons are localized. This problem is most apparent with molecules for which several valid Lewis structures can be drawn. It is clear that none of these structures taken alone adequately describes the electronic structure of the molecule. The concept of resonance was invented to solve this problem. However, even with resonance included, the localized electron model does not describe molecules and ions such as O_3 and NO_3^- in a very satisfying way.

It would seem that the ideal bonding model would be one with the simplicity of the localized electron model but with the delocalization characteristic of the molecular orbital model. We can achieve this by combining the two models to describe molecules that require resonance. Note that for species such as O_3 and NO_3^- the double bond changes position in the resonance structures (see Fig. 9.45). Since a double bond involves one σ and one π bond, there is a σ bond between all bound atoms in each resonance structure. It is really the π bond that has different locations in the various resonance structures.

**FIGURE 9.44**

The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

**FIGURE 9.45**

The resonance structures for O_3 and NO_3^- . Note that it is the double bond that occupies various positions in the resonance structures.

In molecules that require resonance, it is the π bonding that is most clearly delocalized.

Therefore we conclude that the σ bonds in a molecule can be described as being localized with no apparent problems. It is the π bonding that must be treated as being delocalized. Thus, for molecules that require resonance, we will use the localized electron model to describe the σ bonding and the molecular orbital model to describe the π bonding. This allows us to keep the bonding model as simple as possible and yet give a more physically accurate description of such molecules.

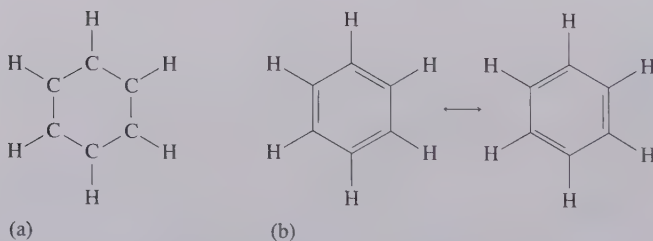
We will illustrate the general method by considering the bonding in benzene, an important industrial chemical that must be handled carefully because it is a known carcinogen. The benzene molecule (C_6H_6) consists of a planar hexagon of carbon atoms with one hydrogen atom bound to each carbon atom, as shown in Fig. 9.46(a). In the molecule all six C—C bonds are known to be equivalent. To explain this fact, the localized electron model must invoke resonance [see Fig. 9.46(b)].

A better description of the bonding in benzene results when we use a combination of the models, as described above. In this description it is assumed that the σ bonds of carbon involve sp^2 orbitals, as shown in Fig. 9.47. These σ bonds are all centered in the plane of the molecule.

Since each carbon atom is sp^2 hybridized, a p orbital perpendicular to the plane of the ring remains on each carbon atom. These six p orbitals can be used to form π molecular orbitals, as shown in Fig. 9.48(a). The electrons in the resulting π molecular orbitals are delocalized above and below the plane of the ring, as shown in Fig. 9.48(b). This gives six equivalent C—C bonds, as required by the known structure of the benzene molecule. The benzene structure is often written as



to indicate the **delocalized π bonding** in the molecule.

**FIGURE 9.46**

(a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon; all atoms are in the same plane. All the C—C bonds are known to be equivalent. (b) Two of the resonance structures for the benzene molecule. The localized electron model must invoke resonance to account for the six equal C—C bonds.

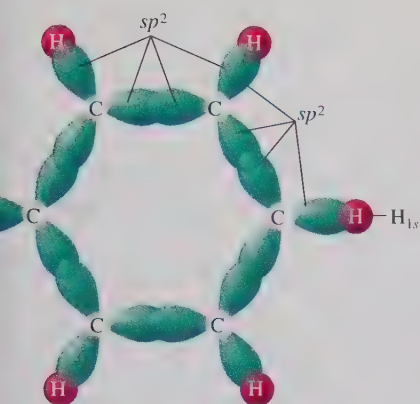


FIGURE 9.47
 σ bonding system in the benzene molecule.

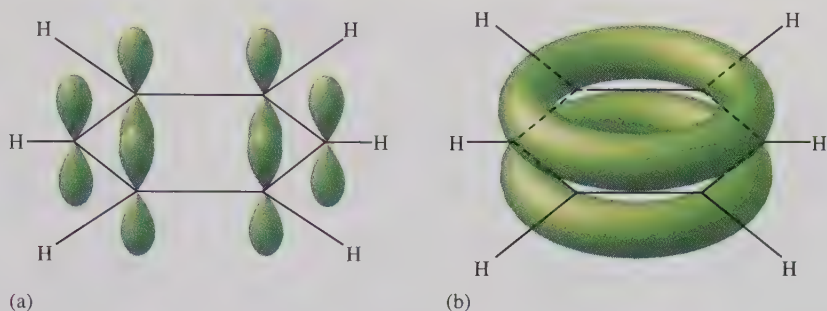


FIGURE 9.48

(a) The π molecular orbital system in benzene is formed by combining the six p orbitals from the six sp^2 hybridized carbon atoms. (b) The electrons in the resulting π molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is represented here.

Very similar treatments can be applied to other planar molecules for which resonance is required by the localized electron model. For example, the NO_3^- ion can be described using the π molecular orbital system shown in Fig. 9.49. In this molecule each atom is assumed to be sp^2 hybridized, which leaves one p orbital on each atom perpendicular to the plane of the ion. These p orbitals can combine to form the π molecular orbital system.

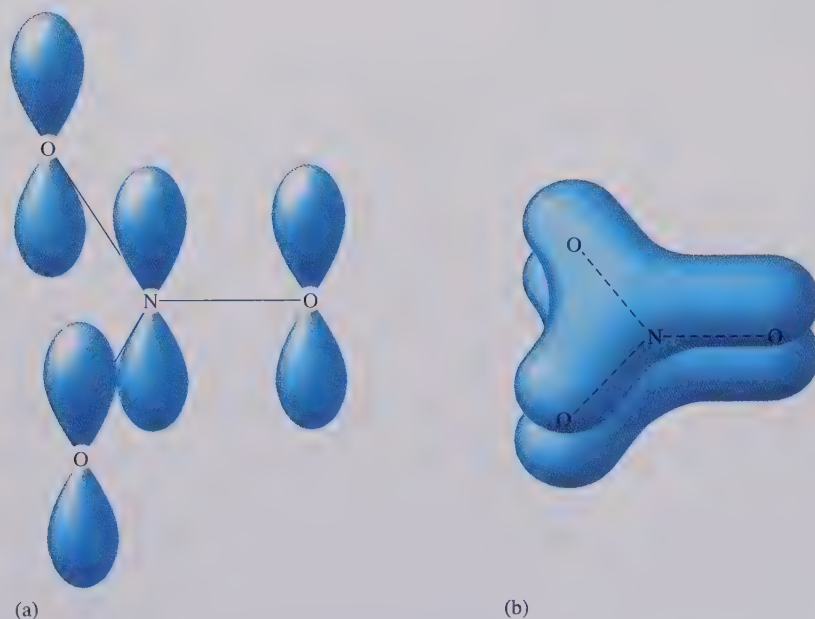


FIGURE 9.49

(a) The p orbitals used to form the π bonding system in the NO_3^- ion. (b) A representation of the delocalization of the electrons in the π molecular orbital system of the NO_3^- ion.

For Review

Key Terms

Section 9.1

hybridization
 sp^3 hybridization
hybrid orbitals
 sp^2 hybridization
sigma (σ) bond
pi (π) bond
 sp hybridization
 dsp^3 hybridization
 d^2sp^3 hybridization

Section 9.2

molecular orbital model
molecular orbital (MO)
sigma (σ) molecular orbital
bonding molecular orbital
antibonding molecular orbital
bond order

Section 9.3

pi (π) molecular orbital
paramagnetism
diamagnetism

Section 9.4

heteronuclear diatomic molecule

Section 9.5

delocalized π bonding

Summary

In this chapter we have emphasized the role of orbitals in the covalent bonding in molecules. The two most useful models are the localized electron model and the molecular orbital model.

In the localized electron model, a molecule is pictured as a group of atoms sharing electron pairs using atomic orbitals. Because the requirements of the molecule are different from those of separated atoms, the original atomic orbitals are combined to form new hybrid orbitals, which are used by the atoms in the molecule. The specific set of hybrid orbitals needed is determined by the arrangement of electron pairs that gives the minimum repulsion. For example, an atom surrounded by four electron pairs requires a tetrahedral arrangement and a set of sp^3 hybrid orbitals; a trigonal planar arrangement requires sp^2 hybridization; and a linear arrangement requires sp hybridization.

When an electron pair is shared in the area centered on a line joining the atoms, the covalent bond is called a σ bond. A π bond occurs when p orbitals overlap in a parallel fashion. The shared electron pair then occupies the space above and below the line joining the bonded atoms.

Multiple bonds involve σ and π bonds. A double bond consists of a σ bond and a π bond; a triple bond involves a σ bond and two π bonds.

In the molecular orbital model for covalent bonding, the molecule is assumed to be a new entity consisting of positively charged nuclei and electrons. We use calculations similar to those used for atoms to determine the allowed orbitals in the molecule. The molecular orbitals are constructed from the valence orbitals of the atoms involved in forming the molecule.

Molecular orbitals are classified in two ways:

1. MOs are classified according to their energy. A bonding MO is an orbital that is lower in energy than the original atomic orbitals. In going from the free atoms to the molecule, electrons occupying bonding MOs are lowered in energy. This favors formation of a stable molecule (bonds are formed). An antibonding MO is an orbital that is higher in energy than the original atomic orbitals. In going from the free atoms to the molecule, electrons in antibonding MOs are raised in energy. These electrons oppose bonding.
2. MOs are classified according to their shape (symmetry). Sigma (σ) molecular orbitals have their electron probability centered about a line passing through the two nuclei. Pi (π) molecular orbitals have their electron probability concentrated above and below the line passing through the nuclei.

Bond order is an index of bond strength:

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

The greater the difference between the number of electrons that are lowered in energy (bonding electrons) and the number of electrons that are raised in energy (antibonding electrons) when the molecule forms, the greater will be the stability of the molecule (the stronger the bonding).

The main strengths of the molecular orbital model are that it correctly predicts the relative bond strength and magnetism of simple diatomic molecules (the correct prediction of the paramagnetism of the oxygen molecule is an important example), it accounts for bond polarity, and it correctly portrays electrons as being delocalized in polyatomic molecules. The main disadvantage of the molecular orbital model is that it is difficult to apply qualitatively to polyatomic molecules.

The concept of resonance is required for certain molecules because the localized electron model incorrectly assumes that electrons are located between a given pair of atoms in a molecule. A more physically accurate description of these molecules can be given by combining the localized electron and molecular orbital models. The σ bonds in these molecules can be regarded as localized, while the π bonding is best described as delocalized.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. What are molecular orbitals? How do they compare with atomic orbitals? Can you tell by the shape of the bonding and antibonding orbitals which is lower in energy? Explain.
2. Explain the difference between the σ and π MOs for homonuclear diatomic molecules. How are bonding and antibonding orbitals different? Why are there two π MOs and one σ MO? Why are the π MOs degenerate?
3. Compare Figs. 9.36 and 9.38. Why are they different? Because B_2 is known to be paramagnetic, the π_{2p} and σ_{2p} molecular orbitals must be switched from the first prediction. What is the rationale for this? Why might one expect the σ_{2p} to be lower in energy than the π_{2p} ? Why can't we use diatomic oxygen to help us decide whether the σ_{2p} or π_{2p} is lower in energy?
4. Which of the following would you expect to be more favorable energetically? Explain.
 - a. An H_2 molecule in which enough energy is added to excite one electron from the bonding to the antibonding MO
 - b. Two separate H atoms
5. Draw the Lewis structure for HCN. Indicate the hybrid orbitals, and draw a picture showing all the bonds between the atoms, labeling each bond as σ or π .
6. Which is the more correct statement: "The methane molecule (CH_4) is a tetrahedral molecule because it is sp^3 hybridized" or "The methane molecule (CH_4) is sp^3 hybridized because it is a tetrahedral molecule"? What, if anything, is the difference between these two statements?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

7. What are the relationships among bond order, bond energy, and bond length? Which of these quantities can be measured?
8. Electrons in σ bonding molecular orbitals are most likely to be found in the region between the two bonded atoms. Why does this arrangement favor bonding? In a σ antibonding orbital, where are the electrons most likely to be found in relation to the nuclei in a bond?
9. What type of experiment can be done to determine if a material is paramagnetic?
10. What type of molecules exhibit delocalized π bonding? Explain.

Exercises

In this section similar exercises are paired.

The Localized Electron Model and Hybrid Orbitals

11. Use the localized electron model to describe the bonding in H_2O .
12. Use the localized electron model to describe the bonding in CCl_4 .
13. Use the localized electron model to describe the bonding in H_2CO (carbon is the central atom).
14. Use the localized electron model to describe the bonding in C_2H_2 (exists as $HCCH$).
15. Give the expected hybridization of the central atom for the molecules or ions in Exercises 61 and 65 from Chapter 8.
16. Give the expected hybridization of the central atom for the molecules or ions in Exercises 62 and 66 from Chapter 8.
17. Give the expected hybridization of the central atom for the molecules or ions in Exercise 63 from Chapter 8.

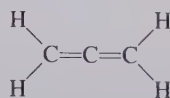
18. Give the expected hybridization of the central atom for the molecules in Exercise 64 from Chapter 8.
19. Give the expected hybridization of the central atom for the molecules in Exercises 81 and 82 from Chapter 8.
20. Give the expected hybridization of the central atom for the molecules in Exercises 83 and 84 from Chapter 8.
21. For each of the following molecules, write the Lewis structure(s), predict the molecular structure (including bond angles), give the expected hybrid orbitals on the central atom, and predict the overall polarity.
- CF_4
 - NF_3
 - OF_2
 - BF_3
 - BeH_2
 - TeF_4
 - AsF_5
 - KrF_2
 - KrF_4
 - SeF_6
 - IF_5
 - IF_3

22. For each of the following molecules or ions that contain sulfur, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybrid orbitals for sulfur.

- SO_2
- SO_3
- $\text{S}_2\text{O}_3^{2-}$
- $\text{S}_2\text{O}_8^{2-}$
- SO_3^{2-}
- SO_4^{2-}
- SF_2
- SF_4
- SF_6
- $\text{F}_3\text{S}-\text{SF}$
- SF_5^+

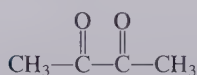
23. Why must all six atoms in C_2H_4 be in the same plane?

24. The allene molecule has the following Lewis structure:

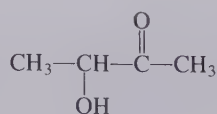


Are all four hydrogen atoms in the same plane? If not, what is their spatial relationship? Explain.

25. Biacetyl and acetoin are added to margarine to make it taste more like butter.



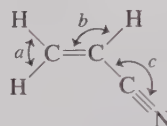
Biacetyl



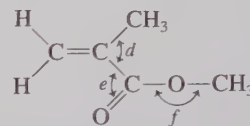
Acetoin

Complete the Lewis structures, predict values for all $\text{C}-\text{C}-\text{O}$ bond angles, and give the hybridization of the carbon atoms in these two compounds. Are the four carbons and two oxygens in biacetyl in the same plane? How many σ bonds and how many π bonds are there in biacetyl and acetoin?

26. Many important compounds in the chemical industry are derivatives of ethylene (C_2H_4). Two of them are acrylonitrile and methyl methacrylate.



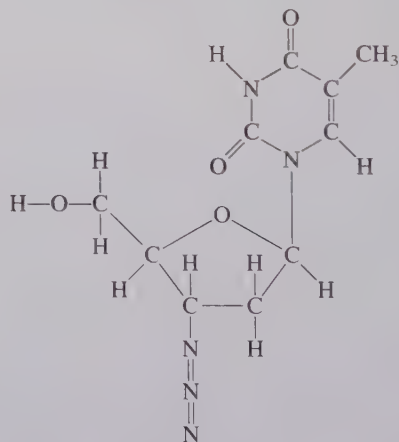
Acrylonitrile



Methyl methacrylate

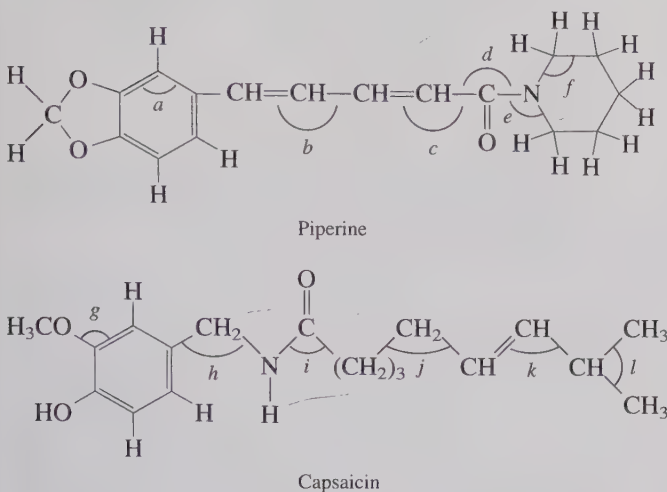
Complete the Lewis structures, showing all lone pairs. Give approximate values for bond angles a through f . Give the hybridization of all carbon atoms. In acrylonitrile, how many of the atoms in the molecule lie in the same plane? How many σ bonds and how many π bonds are there in methyl methacrylate and acrylonitrile?

27. One of the first drugs to be approved for use in treatment of acquired immune deficiency syndrome (AIDS) was azidothymidine (AZT). Complete the Lewis structure for AZT.



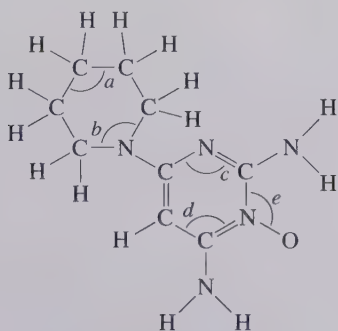
- How many carbon atoms are sp^3 hybridized?
- How many carbon atoms are sp^2 hybridized?
- Which atom is sp hybridized?
- How many σ bonds are in the molecule?
- How many π bonds are in the molecule?
- What is the $\text{N}-\text{N}-\text{N}$ bond angle in the azide ($-\text{N}_3$) group?
- What is the $\text{H}-\text{O}-\text{C}$ bond angle in the side group attached to the five-membered ring?
- What is the hybridization of the oxygen atom in the $-\text{CH}_2\text{OH}$ group?

28. Hot and spicy foods contain molecules that stimulate pain-detecting nerve endings. Two such molecules are piperine and capsaicin:



Piperine is the active compound in white and black pepper, and capsaicin is the active compound in chili peppers. The ring structures in piperine and capsaicin are shorthand notation. Each point where lines meet represents a carbon atom.

- Complete the Lewis structure for piperine and capsaicin showing all lone pairs of electrons.
 - How many carbon atoms are sp , sp^2 , and sp^3 hybridized in each molecule?
 - Which hybrid orbitals are used by the nitrogen atoms in each molecule?
 - Give approximate values for the bond angles marked a through l in the above structures.
29. Minoxidil ($C_9H_{15}N_5O$) is a compound that has been approved as a treatment for some types of male-pattern baldness. An incomplete Lewis structure for minoxidil is



Complete the Lewis structure and answer the following questions.

- Give the hybridization of the five nitrogen atoms in minoxidil.
- Give the hybridization of each of the nine carbon atoms in minoxidil.

- Give approximate values of the bond angles marked a , b , c , d , and e .
- How many σ bonds exist in minoxidil?
- How many π bonds exist in minoxidil?

30. The three most stable oxides of carbon are carbon monoxide (CO), carbon dioxide (CO_2), and carbon suboxide (C_3O_2). The space-filling models for these three compounds are



For each oxide, draw the Lewis structure, predict the molecular structure, and describe the bonding (in terms of the hybrid orbitals for the carbon atoms).

The Molecular Orbital Model

- Which of the following are predicted by the molecular orbital model to be stable diatomic species?
 - H_2^+ , H_2 , H_2^- , H_2^{2-}
 - He_2^{2+} , He_2^+ , He_2
- Which of the following are predicted by the molecular orbital model to be stable diatomic species?
 - N_2^{2-} , O_2^{2-} , F_2^{2-}
 - Be_2 , B_2 , Ne_2
- Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?
 - Li_2
 - C_2
 - S_2
- Acetylene (C_2H_2) can be produced from the reaction of calcium carbide (CaC_2) with water. Use both the localized electron and molecular orbital models to describe the bonding in the acetylide anion (C_2^{2-}).
- Using the molecular orbital model to describe the bonding in O_2^+ , O_2 , O_2^- , and O_2^{2-} , predict the bond orders and the relative bond lengths for these four species. How many unpaired electrons are present in each one?
- Using the molecular orbital model to describe the bonding in F_2^+ , F_2 , and F_2^- , predict the bond orders and the relative bond lengths for these three species. How many unpaired electrons are present in each species?

- Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic? Place the species in order of increasing bond length and bond energy.
 - CO
 - CO^+
 - CO^{2+}

- Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic? Place the species in order of increasing bond length and bond energy.

- a. NO^+
- b. NO
- c. NO^-

39. In which of the following diatomic molecules would the bond strength be expected to weaken as an electron is removed to form the positive charged ion?

- a. H_2
- b. B_2
- c. N_2
- d. OF

40. In terms of the molecular orbital model, which species in each of the following two pairs will most likely be the one to gain an electron? Explain.

- CN or NO
 O_2^{2+} or N_2^{2+}

41. Show how two $2p$ atomic orbitals can combine to form a σ or a π molecular orbital.

42. Show how a hydrogen $1s$ atomic orbital and a fluorine $2p$ atomic orbital overlap to form bonding and antibonding molecular orbitals in the hydrogen fluoride molecule. Are these molecular orbitals σ or π molecular orbitals?

43. Use Figs. 9.43 and 9.44 to answer the following questions.

- a. Would the bonding molecular orbital in HF place greater electron density near the H or the F atom? Why?
- b. Would the bonding molecular orbital have greater fluorine $2p$ character, greater hydrogen $1s$ character, or an equal contribution from both? Why?
- c. Answer the previous two questions for the antibonding molecular orbital in HF.

44. The diatomic molecule OH exists in the gas phase. The bond length and bond energy have been measured to be 97.06 pm and 424.7 kJ/mol, respectively. Assume that the OH molecule is analogous to the HF molecule discussed in the chapter and that molecular orbitals result from the overlap of a lower-energy p_z orbital from oxygen with the higher-energy $1s$ orbital of hydrogen (the O—H bond lies along the z axis).

- a. Which of the two molecular orbitals will have the greater hydrogen $1s$ character?
- b. Can the $2p_x$ orbital of oxygen form molecular orbitals with the $1s$ orbital of hydrogen? Explain.
- c. Knowing that only the $2p$ orbitals of oxygen will interact significantly with the $1s$ orbital of hydrogen, complete the molecular orbital energy-level diagram for OH. Place the correct number of electrons in the energy levels.
- d. Estimate the bond order for OH.
- e. Predict whether the bond order of OH^+ will be greater than, less than, or the same as that of OH. Explain.

45. Describe the bonding in the O_3 molecule and the NO_2^- ion using the localized electron model. How would the molecular orbital model describe the π bonding in these two species?

46. Describe the bonding in the CO_3^{2-} ion using the localized electron model. How would the molecular orbital model describe the π bonding in this species?

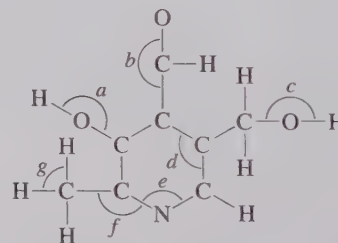
Additional Exercises

47. Draw the Lewis structures, predict the molecular structures, and describe the bonding (in terms of the hybrid orbitals for the central atom) for the following.

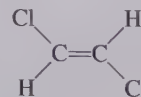
- a. XeO_3
- b. XeO_4
- c. XeOF_4
- d. XeOF_2
- e. XeO_3F_2

48. FCIO_2 and F_3ClO can both gain a fluoride ion to form stable anions. F_3ClO and F_3ClO_2 will both lose a fluoride ion to form stable cations. Draw the Lewis structures and describe the hybrid orbitals used by chlorine in these ions.

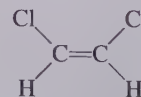
49. Vitamin B_6 is an organic compound whose deficiency in the human body can cause apathy, irritability, and an increased susceptibility to infections. Below is an incomplete Lewis structure for vitamin B_6 . Complete the Lewis structure and answer the following questions. *Hint:* Vitamin B_6 can be classified as an organic compound (a compound based on carbon atoms). The majority of Lewis structures for simple organic compounds have all atoms with a formal charge of zero. Therefore, add lone pairs and multiple bonds to the structure below to give each atom a formal charge of zero.



- a. How many σ bonds and π bonds exist in vitamin B_6 ?
 - b. Give approximate values for the bond angles marked a through g in the structure.
 - c. How many carbon atoms are sp^2 hybridized?
 - d. How many carbon, oxygen, and nitrogen atoms are sp^3 hybridized?
 - e. Does vitamin B_6 exhibit delocalized π bonding? Explain.
50. Using bond energies from Table 8.4, estimate the barrier to rotation about a carbon–carbon double bond. To do this, consider what must happen to go from



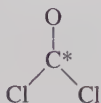
to



in terms of making and breaking chemical bonds; that is, what must happen in terms of the π bond?

51. Complete the Lewis structures of the following molecules. Predict the molecular structure, polarity, bond angles, and hybrid orbitals used by the atoms marked by asterisks for each molecule.

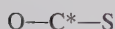
a. COCl_2



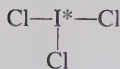
b. N_2F_2



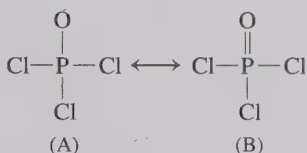
c. COS



d. ICl_3



52. Complete the following resonance structures for POCl_3 .



- Would you predict the same molecular structure from each resonance structure?
 - What is the hybridization of P in each structure?
 - What orbitals can the P atom use to form the π bond in structure B?
 - Which resonance structure would be favored on the basis of formal charges?
53. The N_2O molecule is linear and polar.
- On the basis of this experimental evidence, which arrangement, NNO or NON , is correct? Explain your answer.
 - On the basis of your answer to part a, write the Lewis structure of N_2O (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.
 - How would the multiple bonding in $:\text{N}\equiv\text{N}-\ddot{\text{O}}:$ be described in terms of orbitals?
54. Describe the bonding in NO^+ , NO^- , and NO using both the localized electron and molecular orbital models. Account for any discrepancies between the two models.
55. Describe the bonding in the first excited state of N_2 (the one closest in energy to the ground state) using the molecular orbital model. What differences do you expect in the properties of the molecule in the ground state as compared to the first excited state? (An excited state of a molecule corresponds to

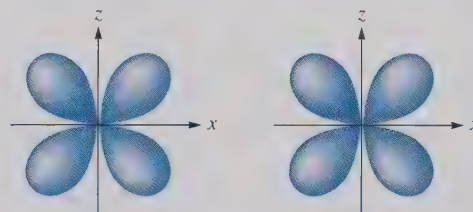
an electron arrangement other than that giving the lowest possible energy.)

56. A Lewis structure obeying the octet rule can be drawn for O_2 as follows:



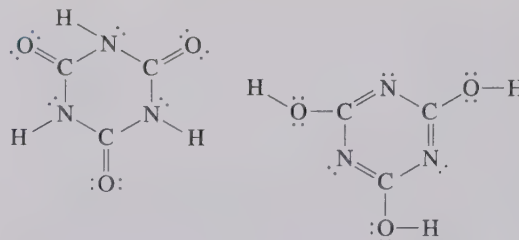
Use the molecular orbital energy-level diagram for O_2 to show that the above Lewis structure corresponds to an excited state.

57. Using an MO energy-level diagram, would you expect F_2 to have a lower or higher first ionization energy than atomic fluorine? Why?
58. What type of molecular orbital would result from the combination of two d_{xz} atomic orbitals shown below? Assume the x -axis is the internuclear axis.

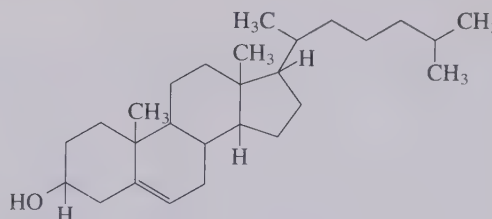


Challenge Problems

59. Two structures can be drawn by cyanuric acid:

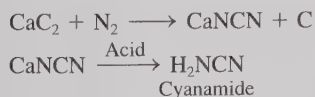


- Are these two structures the same molecule? Explain.
 - Give the hybridization of the carbon and nitrogen atoms in each structure.
 - Use bond energies (Table 8.4) to predict which form is more stable; that is, which contains the strongest bonds?
60. Cholesterol ($\text{C}_{27}\text{H}_{46}\text{O}$) has the following structure:

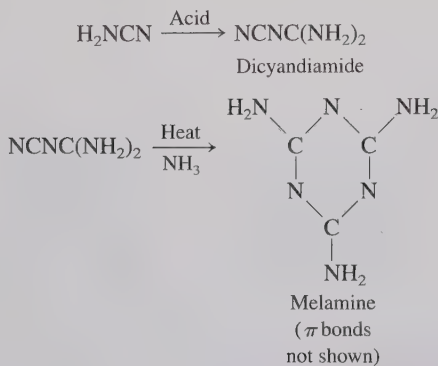


In such shorthand structures, each point where lines meet represents a carbon atom and most H atoms are not shown. Draw the complete structure showing all carbon and hydrogen atoms. (There will be four bonds to each carbon atom.) Indicate which carbon atoms use sp^2 or sp^3 hybrid orbitals. Are all carbon atoms in the same plane, as implied by the structure?

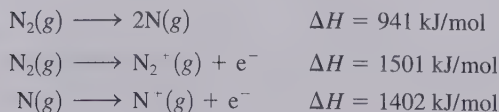
61. Cyanamide (H_2NCN), an important industrial chemical, is produced by the following steps:



Calcium cyanamide (CaNCN) is used as a direct-application fertilizer, weed killer, and cotton defoliant. It is also used to make cyanamide, dicyandiamide, and melamine plastics:

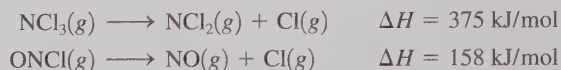


- Write Lewis structures for NCN^{2-} , H_2NCN , dicyandiamide, and melamine, including resonance structures where appropriate.
 - Give the hybridization of the C and N atoms in each species.
 - How many σ bonds and how many π bonds are in each species?
 - Is the ring in melamine planar?
 - There are three different C—N bond distances in dicyandiamide, $\text{NCNC}(\text{NH}_2)_2$, and the molecule is nonlinear. Of all the resonance structures you drew for this molecule, predict which should be the most important.
62. In Exercise 67 in Chapter 8, the Lewis structures for benzene (C_6H_6) were drawn. Using one of the Lewis structures, estimate ΔH_f° for $\text{C}_6\text{H}_6(g)$ using bond energies and given that the standard enthalpy of formation of $\text{C}(g)$ is 717 kJ/mol. The experimental ΔH_f° value of $\text{C}_6\text{H}_6(g)$ is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated ΔH_f° value for $\text{C}_6\text{H}_6(g)$.
63. A flask containing gaseous N_2 is irradiated with 25-nm light.
- Using the following information, indicate what species can form in the flask during irradiation.



- What range of wavelengths will produce atomic nitrogen in the flask but will not produce any ions?
- Explain why the first ionization energy of N_2 (1501 kJ/mol) is greater than the first ionization energy of atomic nitrogen (1402 kJ/mol).

64. As compared with CO and O_2 , CS and S_2 are very unstable molecules. Give an explanation based on the relative abilities of the sulfur and oxygen atoms to form π bonds.
65. Values of measured bond energies may vary greatly depending on the molecule studied. Consider the following reactions:



Rationalize the difference in the values of ΔH for these reactions, even though each reaction appears to involve only the breaking of one N—Cl bond. (*Hint*: Consider the bond order of the NO bond in ONCl and in NO.)

66. Use the MO model to explain the bonding in BeH_2 . When constructing the MO energy-level diagram, assume that the Be's 1s electrons are not involved in bond formation.
67. Carbon monoxide (CO) forms bonds to a variety of metals and metal ions. Its ability to bond to iron in hemoglobin is the reason that CO is so toxic. The bond carbon monoxide forms to metals is through the carbon atom:



- On the basis of electronegativities, would you expect the carbon atom or the oxygen atom to form bonds to metals?
- Assign formal charges to the atoms in CO. Which atom would you expect to bond to a metal on this basis?
- In the MO model, bonding MOs place more electron density near the more electronegative atom. (See the HF molecule, Figs. 9.43 and 9.44.) Antibonding MOs place more electron density near the less electronegative atom in the diatomic molecule. Use the MO model to predict which atom of carbon monoxide should form bonds to metals.



Media Activities

- Open the Chapter 9 Visualizations on the student CD and view the sp^3 , sp^2 , and sp hybridization material. Which hybridization is always used for a tetrahedral arrangement of electron pairs? For a trigonal planar arrangement? For a linear arrangement? What's wrong with the statement, "The methane molecule (CH_4) is a tetrahedral molecule because it is sp^3 hybridized"?
- View the s -Orbitals/bonding and Antibonding Visualization on the student CD. Why is the bonding orbital lower in energy as compared to the separate atoms? Why is the antibonding orbital higher in energy? Open the Molecular Orbitals in H_2 Understanding Concepts activity and read through the introduction. What would be the bond order for the H_2^+ ion? For the H_2^- ion? Using MO theory, explain why He_2 molecules don't form.

3. a. When MO theory is applied to Row 2 and heavier elements, the p orbitals are used to form molecular orbitals. A π orbital is one type of molecular orbital that can form from a p orbital. Open the orbitals in H₂ Understanding Concepts activity and read about π bonding and π antibonding molecular orbitals. If the x -axis is the internuclear axis (the axis that goes through both nuclei of a diatomic molecule), which p orbitals form the π bonding and π antibonding orbitals?
4. What is a paramagnetic molecule? A diamagnetic molecule? What do you look for in the molecular orbital electron configuration to determine the magnetic properties? Is N₂ paramagnetic or diamagnetic? How about O₂? Check your answer by opening the Magnetic Properties of Liquid Nitrogen and Oxygen Visualization. The fact that B₂ is paramagnetic results in the changing of the expected molecular orbital energy level diagram. Explain why this was necessary.
5. Draw all the possible resonance structures for NO₃⁻. What is the hybridization of the central nitrogen atom? Open the pi Bond Visualization to view the π bonding system in NO₃⁻. All the nitrogen-oxygen bonds are equivalent in NO₃⁻. Would you expect the N—O bond strength to be that of a single bond on a double bond, or something else? Explain.
6. Test your understanding of Chapter 9 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

Appendixes

Appendix One Mathematical Procedures

A1.1 Exponential Notation

The numbers characteristic of scientific measurements are often very large or very small; thus it is convenient to express them using powers of 10. For example, the number 1,300,000 can be expressed as 1.3×10^6 , which means multiply 1.3 by 10 six times, or

$$1.3 \times 10^6 = 1.3 \times \underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6 = 1 \text{ million}}$$

Note that each multiplication by 10 moves the decimal point one place to the right:

$$\begin{aligned} 1.3 \times 10 &= 13. \\ 13 \times 10 &= 130. \\ 130 \times 10 &= 1300. \\ &\vdots \end{aligned}$$

Thus the easiest way to interpret the notation 1.3×10^6 is that it means move the decimal point in 1.3 to the right six times:

$$1.3 \times 10^6 = \underbrace{1\,3\,0\,0\,0\,0\,0}_{1\,2\,3\,4\,5\,6} = 1,300,000$$

Using this notation, the number 1985 can be expressed as 1.985×10^3 . Note that the usual convention is to write the number that appears before the power of 10 as a number between 1 and 10. To end up with the number 1.985, which is between 1 and 10, we had to move the decimal point three places to the left. To compensate for that, we must multiply by 10^3 , which says that to get the intended number we start with 1.985 and move the decimal point three places to the right; that is:

$$1.985 \times 10^3 = \underbrace{1\,9\,8\,5.}_{1\,2\,3}$$

Some other examples are given below.

Number	Exponential Notation
5.6	5.6×10^0 or 5.6×1
39	3.9×10^1
943	9.43×10^2
1126	1.126×10^3

So far we have considered numbers greater than 1. How do we represent a number such as 0.0034 in exponential notation? We start with a number between 1 and 10 and *divide* by the appropriate power of 10:

$$0.0034 = \frac{3.4}{10 \times 10 \times 10} = \frac{3.4}{10^3} = 3.4 \times 10^{-3}$$

Division by 10 moves the decimal point one place to the *left*. Thus the number

$$\begin{array}{cccccccc} 0. & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 4 \\ & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \swarrow & \\ & 7 & 6 & 5 & 4 & 3 & 2 & 1 & \end{array}$$

can be written as 1.4×10^{-7} .

To summarize, we can write any number in the form

$$N \times 10^{\pm n}$$

where N is between 1 and 10 and the exponent n is an integer. If the sign preceding n is positive, it means the decimal point in N should be moved n places to the right. If a negative sign precedes n , the decimal point in N should be moved n places to the left.

Multiplication and Division

When two numbers expressed in exponential notation are multiplied, the initial numbers are multiplied and the exponents of 10 are added:

$$(M \times 10^m)(N \times 10^n) = (MN) \times 10^{m+n}$$

For example (to two significant figures, as required),

$$(3.2 \times 10^4)(2.8 \times 10^3) = 9.0 \times 10^7$$

When the numbers are multiplied, if a result greater than 10 is obtained for the initial number, the decimal point is moved one place to the left and the exponent of 10 is increased by 1:

$$\begin{aligned} (5.8 \times 10^2)(4.3 \times 10^8) &= 24.9 \times 10^{10} \\ &= 2.49 \times 10^{11} \\ &= 2.5 \times 10^{11} \quad (\text{two significant figures}) \end{aligned}$$

Division of two numbers expressed in exponential notation involves normal division of the initial numbers and *subtraction* of the exponent of the divisor from that of the dividend. For example,

$$\frac{4.8 \times 10^8}{\underbrace{2.1 \times 10^3}_{\text{Divisor}}} = \frac{4.8}{2.1} \times 10^{(8-3)} = 2.3 \times 10^5$$

If the initial number resulting from the division is less than 1, the decimal point is moved one place to the right and the exponent of 10 is decreased by 1. For example,

$$\begin{aligned} \frac{6.4 \times 10^3}{8.3 \times 10^5} &= \frac{6.4}{8.3} \times 10^{(3-5)} = 0.77 \times 10^{-2} \\ &= 7.7 \times 10^{-3} \end{aligned}$$

Addition and Subtraction

To add or subtract numbers expressed in exponential notation, *the exponents of the numbers must be the same*. For example, to add 1.31×10^5 and 4.2×10^4 , we must rewrite one number so that the exponents of both are the same. The number

1.31×10^5 can be written 13.1×10^4 , since moving the decimal point one place to the right can be compensated for by decreasing the exponent by 1. Now we can add the numbers:

$$\begin{array}{r} 13.1 \times 10^4 \\ + 4.2 \times 10^4 \\ \hline 17.3 \times 10^4 \end{array}$$

In correct exponential notation the result is expressed as 1.73×10^5 .

To perform addition or subtraction with numbers expressed in exponential notation, only the initial numbers are added or subtracted. The exponent of the result is the same as those of the numbers being added or subtracted. To subtract 1.8×10^2 from 8.99×10^3 , we write

$$\begin{array}{r} 8.99 \times 10^3 \\ - 0.18 \times 10^3 \\ \hline 8.81 \times 10^3 \end{array}$$

Powers and Roots

When a number expressed in exponential notation is taken to some power, the initial number is taken to the appropriate power and the exponent of 10 is multiplied by that power:

$$(N \times 10^n)^m = N^m \times 10^{m \cdot n}$$

For example,*

$$\begin{aligned} (7.5 \times 10^2)^3 &= 7.5^3 \times 10^{3 \cdot 2} \\ &= 422 \times 10^6 \\ &= 4.22 \times 10^8 \\ &= 4.2 \times 10^8 \quad (\text{two significant figures}) \end{aligned}$$

When a root is taken of a number expressed in exponential notation, the root of the initial number is taken and the exponent of 10 is divided by the number representing the root:

$$\sqrt[n]{N \times 10^n} = (n \times 10^n)^{1/2} = \sqrt{N} \times 10^{n/2}$$

For example,

$$\begin{aligned} (2.9 \times 10^6)^{1/2} &= \sqrt{2.9} \times 10^{6/2} \\ &= 1.7 \times 10^3 \end{aligned}$$

Because the exponent of the result must be an integer, we may sometimes have to change the form of the number so that the power divided by the root equals an integer. For example,

$$\begin{aligned} \sqrt{1.9 \times 10^3} &= (1.9 \times 10^3)^{1/2} = (0.19 \times 10^4)^{1/2} \\ &= \sqrt{0.19} \times 10^2 \\ &= 0.44 \times 10^2 \\ &= 4.4 \times 10^1 \end{aligned}$$

*Refer to the instruction booklet for your calculator for directions concerning how to take roots and powers of numbers.

In this case, we moved the decimal point one place to the left and increased the exponent from 3 to 4 to make $n/2$ an integer.

The same procedure is followed for roots other than square roots. For example,

$$\begin{aligned}\sqrt[3]{6.9 \times 10^5} &= (6.9 \times 10^5)^{1/3} = (0.69 \times 10^6)^{1/3} \\ &= \sqrt[3]{0.69} \times 10^2 \\ &= 0.88 \times 10^2 \\ &= 8.8 \times 10^1\end{aligned}$$

and

$$\begin{aligned}\sqrt[3]{4.6 \times 10^{10}} &= (4.6 \times 10^{10})^{1/3} = (46 \times 10^9)^{1/3} \\ &= \sqrt[3]{46} \times 10^3 \\ &= 3.6 \times 10^3\end{aligned}$$

A1.2 Logarithms

A logarithm is an exponent. Any number N can be expressed as follows:

$$N = 10^x$$

For example,

$$\begin{aligned}1000 &= 10^3 \\ 100 &= 10^2 \\ 10 &= 10^1 \\ 1 &= 10^0\end{aligned}$$

The common, or base 10, logarithm of a number is the power to which 10 must be taken to yield the number. Thus, since $1000 = 10^3$,

$$\log 1000 = 3$$

Similarly,

$$\begin{aligned}\log 100 &= 2 \\ \log 10 &= 1 \\ \log 1 &= 0\end{aligned}$$

For a number between 10 and 100, the required exponent of 10 will be between 1 and 2. For example, $65 = 10^{1.8129}$; that is, $\log 65 = 1.8129$. For a number between 100 and 1000, the exponent of 10 will be between 2 and 3. For example, $650 = 10^{2.8129}$ and $\log 650 = 2.8129$.

A number N greater than 0 and less than 1 can be expressed as follows:

$$N = 10^{-x} = \frac{1}{10^x}$$

For example,

$$\begin{aligned}0.001 &= \frac{1}{1000} = \frac{1}{10^3} = 10^{-3} \\ 0.01 &= \frac{1}{100} = \frac{1}{10^2} = 10^{-2} \\ 0.1 &= \frac{1}{10} = \frac{1}{10^1} = 10^{-1}\end{aligned}$$

Thus

$$\log 0.001 = -3$$

$$\log 0.01 = -2$$

$$\log 0.1 = -1$$

Although common logs are often tabulated, the most convenient method for obtaining such logs is to use an electronic calculator. On most calculators the number is first entered and then the log key is punched. The log of the number then appears in the display.* Some examples are given below. You should reproduce these results on your calculator to be sure that you can find common logs correctly.

Number	Common Log
36	1.56
1849	3.2669
0.156	-0.807
1.68×10^{-5}	-4.775

Note that the number of digits after the decimal point in a common log is equal to the number of significant figures in the original number.

Since logs are simply exponents, they are manipulated according to the rules for exponents. For example, if $A = 10^x$ and $B = 10^y$, then their product is

$$A \cdot B = 10^x \cdot 10^y = 10^{x+y}$$

and

$$\log AB = x + y = \log A + \log B$$

For division, we have

$$\frac{A}{B} = \frac{10^x}{10^y} = 10^{x-y}$$

and

$$\log \frac{A}{B} = x - y = \log A - \log B$$

For a number raised to a power, we have

$$A^n = (10^x)^n = 10^{nx}$$

and

$$\log A^n = nx = n \log A$$

It follows that

$$\log \frac{1}{A^n} = \log A^{-n} = -n \log A$$

or, for $n = 1$,

$$\log \frac{1}{A} = -\log A$$

*Refer to the instruction booklet for your calculator for the exact sequence to obtain logarithms.

When a common log is given, to find the number it represents, we must carry out the process of exponentiation. For example, if the log is 2.673, then $N = 10^{2.673}$. The process of exponentiation is also called taking the antilog, or the inverse logarithm. This operation is usually carried out on calculators in one of two ways. The majority of calculators require that the log be entered first and then the keys $\boxed{\text{INV}}$ and $\boxed{\text{LOG}}$ pressed in succession. For example, to find $N = 10^{2.673}$ we enter 2.673 and then press $\boxed{\text{INV}}$ and $\boxed{\text{LOG}}$. The number 471 will be displayed; that is, $N = 471$. Some calculators have a $\boxed{10^x}$ key. In that case, the log is entered first and then the $\boxed{10^x}$ key is pressed. Again, the number 471 will be displayed.

Natural logarithms, another type of logarithm, are based on the number 2.7183, which is referred to as e . In this case, a number is represented as $N = e^x = 2.7183^x$. For example,

$$N = 7.15 = e^x$$

$$\ln 7.15 = x = 1.967$$

To find the natural log of a number using a calculator, the number is entered and then the $\boxed{\ln}$ key is pressed. Use the following examples to check your technique for finding natural logs with your calculator:

Number (e^x)	Natural Log(x)
784	6.664
1.61×10^3	7.384
1.00×10^{-7}	-16.118
1.00	0

If a natural logarithm is given, to find the number it represents, exponentiation to the base e (2.7183) must be carried out. With many calculators this is done using a key marked $\boxed{e^x}$ (the natural log is entered, with the correct sign, and then the $\boxed{e^x}$ key is pressed). The other common method for exponentiation to base e is to enter the natural log and then press the $\boxed{\text{INV}}$ and $\boxed{\ln}$ keys in succession. The following examples will help you check your technique:

$\ln N(x)$	$N(e^x)$
3.256	25.9
-5.169	5.69×10^{-3}
13.112	4.95×10^5

Since natural logarithms are simply exponents, they are also manipulated according to the mathematical rules for exponents given above for common logs.

A1.3 Graphing Functions

In interpreting the results of a scientific experiment, it is often useful to make a graph. If possible, the function to be graphed should be in a form that gives a straight line. The equation for a straight line (a *linear equation*) can be represented by the general form

$$y = mx + b$$

where y is the *dependent variable*, x is the *independent variable*, m is the *slope*, and b is the *intercept* with the y axis.

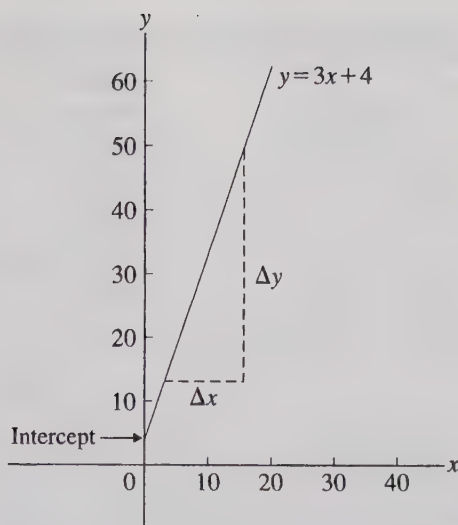


FIGURE A.1
Graph of the linear equation
 $y = 3x + 4$.

To illustrate the characteristics of a linear equation, the function $y = 3x + 4$ is plotted in Fig. A.1. For this equation $m = 3$ and $b = 4$. Note that the y intercept occurs when $x = 0$. In this case the intercept is 4, as can be seen from the equation ($b = 4$).

The slope of a straight line is defined as the ratio of the rate of change in y to that in x :

$$m = \text{slope} = \frac{\Delta y}{\Delta x}$$

For the equation $y = 3x + 4$, y changes three times as fast as x (since x has a coefficient of 3). Thus the slope in this case is 3. This can be verified from the graph. For the triangle shown in Fig. A.1,

$$\Delta y = 34 - 10 = 24 \quad \text{and} \quad \Delta x = 10 - 2 = 8$$

Thus

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{24}{8} = 3$$

The preceding example illustrates a general method for obtaining the slope of a line from the graph of that line. Simply draw a triangle with one side parallel to the y axis and the other parallel to the x axis as shown in Fig. A.1. Then determine the lengths of the sides to give Δy and Δx , respectively, and compute the ratio $\Delta y/\Delta x$.

Sometimes an equation that is not in standard form can be changed to the form $y = mx + b$ by rearrangement or mathematical manipulation. An example is the equation $k = Ae^{-E_a/RT}$ described in Section 12.7, where A , E_a , and R are constants; k is the dependent variable; and $1/T$ is the independent variable. This equation can be changed to standard form by taking the natural logarithm of both sides,

$$\ln k = \ln Ae^{-E_a/RT} = \ln A + \ln e^{-E_a/RT} = \ln A - \frac{E_a}{RT}$$

noting that the log of a product is equal to the sum of the logs of the individual terms and that the natural log of $e^{-E_a/RT}$ is simply the exponent $-E_a/RT$. Thus, in

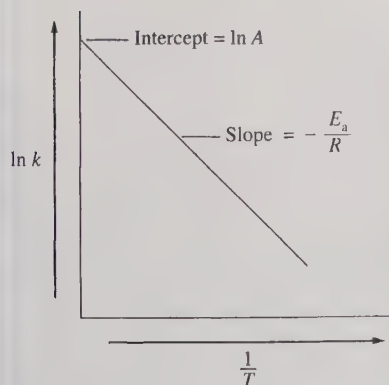


FIGURE A.2
Graph of $\ln k$ versus $1/T$.

TABLE A.1 Some Useful Linear Equations in Standard Form

Equation ($y = mx + b$)	What Is Plotted (y vs. x)	Slope (m)	Intercept (b)	Section in Text
$[A] = -kt + [A]_0$	$[A]$ vs. t	$-k$	$[A]_0$	12.4
$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs. t	$-k$	$\ln[A]_0$	12.4
$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs. t	k	$\frac{1}{[A]_0}$	12.4
$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C$	$\ln P_{\text{vap}}$ vs. $\frac{1}{T}$	$-\frac{\Delta H_{\text{vap}}}{R}$	C	10.8

standard form, the equation $k = Ae^{-E_a/RT}$ is written

$$\underbrace{\ln k}_{y'} = \underbrace{-\frac{E_a}{R}}_m \underbrace{\left(\frac{1}{T} \right)}_x + \underbrace{\ln A}_b$$

A plot of $\ln k$ versus $1/T$ (see Fig. A.2) gives a straight line with slope $-E_a/R$ and intercept $\ln A$.

Other linear equations that are useful in the study of chemistry are listed in standard form in Table A.1.

A1.4 Solving Quadratic Equations

A *quadratic equation*, a polynomial in which the highest power of x is 2, can be written as

$$ax^2 + bx + c = 0$$

One method for finding the two values of x that satisfy a quadratic equation is to use the *quadratic formula*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where a , b , and c are the coefficients of x^2 and x and the constant, respectively. For example, in determining $[\text{H}^+]$ in a solution of $1.0 \times 10^{-4} M$ acetic acid the following expression arises:

$$1.8 \times 10^{-5} = \frac{x^2}{1.0 \times 10^{-4} - x}$$

which yields

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

where $a = 1$, $b = 1.8 \times 10^{-5}$, and $c = -1.8 \times 10^{-9}$. Using the quadratic formula, we have

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} - (4)(1)(-1.8 \times 10^{-9})}}{2(1)} \end{aligned}$$

$$\begin{aligned}
 &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} + 7.2 \times 10^{-9}}}{2} \\
 &= \frac{-1.8 \times 10^{-5} \pm \sqrt{7.5 \times 10^{-9}}}{2} \\
 &= \frac{-1.8 \times 10^{-5} \pm 8.7 \times 10^{-5}}{2}
 \end{aligned}$$

Thus

$$x = \frac{6.9 \times 10^{-5}}{2} = 3.5 \times 10^{-5}$$

and

$$x = \frac{-10.5 \times 10^{-5}}{2} = -5.2 \times 10^{-5}$$

Note that there are two roots, as there always will be, for a polynomial in x^2 . In this case x represents a concentration of H^+ (see Section 14.3). Thus the positive root is the one that solves the problem, since a concentration cannot be a negative number.

A second method for solving quadratic equations is by *successive approximations*, a systematic method of trial and error. A value of x is guessed and substituted into the equation everywhere x (or x^2) appears, except for one place. For example, for the equation

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

we might guess $x = 2 \times 10^{-5}$. Substituting that value into the equation gives

$$x^2 + (1.8 \times 10^{-5})(2 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

or

$$x^2 = 1.8 \times 10^{-9} - 3.6 \times 10^{-10} = 1.4 \times 10^{-9}$$

Thus

$$x = 3.7 \times 10^{-5}$$

Note that the guessed value of $x(2 \times 10^{-5})$ is not the same as the value of x that is calculated (3.7×10^{-5}) after inserting the estimated value. This means that $x = 2 \times 10^{-5}$ is not the correct solution, and we must try another guess. We take the calculated value (3.7×10^{-5}) as our next guess:

$$\begin{aligned}
 x^2 + (1.8 \times 10^{-5})(3.7 \times 10^{-5}) - 1.8 \times 10^{-9} &= 0 \\
 x^2 = 1.8 \times 10^{-9} - 6.7 \times 10^{-10} &= 1.1 \times 10^{-9}
 \end{aligned}$$

Thus

$$x = 3.3 \times 10^{-5}$$

Now we compare the two values of x again:

$$\text{Guessed: } x = 3.7 \times 10^{-5}$$

$$\text{Calculated: } x = 3.3 \times 10^{-5}$$

These values are closer but not close enough. Next we try 3.3×10^{-5} as our guess:

$$\begin{aligned}
 x^2 + (1.8 \times 10^{-5})(3.3 \times 10^{-5}) - 1.8 \times 10^{-9} &= 0 \\
 x^2 = 1.8 \times 10^{-9} - 5.9 \times 10^{-10} &= 1.2 \times 10^{-9}
 \end{aligned}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Again we compare:

$$\text{Guessed: } x = 3.3 \times 10^{-5}$$

$$\text{Calculated: } x = 3.5 \times 10^{-5}$$

Next we guess $x = 3.5 \times 10^{-5}$ to give

$$x^2 + (1.8 \times 10^{-5})(3.5 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

$$x^2 = 1.8 \times 10^{-9} - 6.3 \times 10^{-10} = 1.2 \times 10^{-9}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Now the guessed value and the calculated value are the same; we have found the correct solution. Note that this agrees with one of the roots found with the quadratic formula in the first method above.

To further illustrate the method of successive approximations, we will solve Sample Exercise 14.17 using this procedure. In solving for $[H^+]$ for $0.010 M H_2SO_4$, we obtain the following expression:

$$1.2 \times 10^{-2} = \frac{x(0.010 + x)}{0.010 - x}$$

which can be rearranged to give

$$x = (1.2 \times 10^{-2}) \left(\frac{0.010 - x}{0.010 + x} \right)$$

We will guess a value for x , substitute it into the right side of the equation, and then calculate a value for x . In guessing a value for x , we know it must be less than 0.010, since a larger value will make the calculated value for x negative and the guessed and calculated values will never match. We start by guessing $x = 0.005$.

The results of the successive approximations are shown in the following table:

Trial	Guessed Value for x	Calculated Value for x
1	0.0050	0.0040
2	0.0040	0.0051
3	0.00450	0.00455
4	0.00452	0.00453

Note that the first guess was close to the actual value and that there was oscillation between 0.004 and 0.005 for the guessed and calculated values. For trial 3, an average of these values was used as the guess, and this led rapidly to the correct value (0.0045 to the correct number of significant figures). Also, note that it is useful to carry extra digits until the correct value is obtained. That value can then be rounded off to the correct number of significant figures.

The method of successive approximations is especially useful for solving polynomials containing x to a power of 3 or higher. The procedure is the same as for quadratic equations: Substitute a guessed value for x into the equation for every x term but one, and then solve for x . Continue this process until the guessed and calculated values agree.

A1.5 Uncertainties in Measurements

Like all the physical sciences, chemistry is based on the results of measurements. Every measurement has an inherent uncertainty, so if we are to use the results of measurements to reach conclusions, we must be able to estimate the sizes of these uncertainties.

For example, the specification for a commercial 500-mg acetaminophen (the active painkiller in Tylenol) tablet is that each batch of tablets must contain 450 to 550 mg of acetaminophen per tablet. Suppose that chemical analysis gave the following results for a batch of acetaminophen tablets: 428 mg, 479 mg, 442 mg, and 435 mg. How can we use these results to decide if the batch of tablets meets the specification? Although the details of how to draw such conclusions from measured data are beyond the scope of this text, we will consider some aspects of how this is done. We will focus here on the types of experimental uncertainty, the expression of experimental results, and a simplified method for estimating experimental uncertainty when several types of measurement contribute to the final result.

Types of Experimental Error

There are two types of experimental uncertainty (error). A variety of names are applied to these types of errors:

Precision $\longleftrightarrow$ random error $\equiv$ indeterminate error

Accuracy $\longleftrightarrow$ systematic error $\equiv$ determinate error

The difference between the two types of error is well illustrated by the attempts to hit a target shown in Fig. 1.7 in Chapter 1.

Random error is associated with every measurement. To obtain the last significant figure for any measurement, we must always make an estimate. For example, we interpolate between the marks on a meter stick, a buret, or a balance. The precision of replicate measurements (repeated measurements of the same type) reflects the size of the random errors. Precision refers to the reproducibility of replicate measurements.

The accuracy of a measurement refers to how close it is to the true value. An inaccurate result occurs as a result of some flaw (systematic error) in the measurement: the presence of an interfering substance, incorrect calibration of an instrument, operator error, and so on. The goal of chemical analysis is to eliminate systematic error, but random errors can only be minimized. In practice, an experiment is almost always done to find an unknown value (the true value is not known—someone is trying to obtain that value by doing the experiment). In this case the precision of several replicate determinations is used to assess the accuracy of the result. The results of the replicate experiments are expressed as an average (which we assume is close to the true value) with an error limit that gives some indication of how close the average value may be to the true value. The error limit represents the uncertainty of the experimental result.

Expression of Experimental Results

If we perform several measurements, such as for the analysis for acetaminophen in painkiller tablets, the results should express two things: the average of the measurements and the size of the uncertainty.

There are two common ways of expressing an average: the mean and the median. The mean ($\bar{x}$) is the arithmetic average of the results, or

$$\text{Mean} = \bar{x} = \sum_{i=1}^n \frac{x_i}{n} = \frac{x_1 + x_2 + \cdots + x_n}{n}$$

where Σ means take the sum of the values. The mean is equal to the sum of all the measurements divided by the number of measurements. For the acetaminophen results given previously, the mean is

$$\bar{x} = \frac{428 + 479 + 442 + 435}{4} = 446 \text{ mg}$$

The median is the value that lies in the middle among the results. Half the measurements are above the median and half are below the median. For results of 465 mg, 485 mg, and 492 mg, the median is 485 mg. When there is an even number of results, the median is the average of the two middle results. For the acetaminophen results, the median is

$$\frac{442 + 435}{2} = 438 \text{ mg}$$

There are several advantages to using the median. If a small number of measurements is made, one value can greatly affect the mean. Consider the results for the analysis of acetaminophen: 428 mg, 479 mg, 442 mg, and 435 mg. The mean is 446 mg, which is larger than three of the four weights. The median is 438 mg, which lies near the three values that are relatively close to one another.

In addition to expressing an average value for a series of results, we must express the uncertainty. This usually means expressing either the precision of the measurements or the observed range of the measurements. The range of a series of measurements is defined by the smallest value and the largest value. For the analytical results on the acetaminophen tablets, the range is from 428 mg to 479 mg. Using this range, we can express the results by saying that the true value lies between 428 mg and 479 mg. That is, we can express the amount of acetaminophen in a typical tablet as 446 ± 33 mg, where the error limit is chosen to give the observed range (approximately).

The most common way to specify precision is by the standard deviation, s , which for a small number of measurements is given by the formula

$$s = \left[\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1} \right]^{1/2}$$

where x_i is an individual result, $\bar{x}$ is the average (either mean or median), and n is the total number of measurements. For the acetaminophen example, we have

$$s = \left[\frac{(428 - 446)^2 + (479 - 446)^2 + (442 - 446)^2 + (435 - 446)^2}{4 - 1} \right]^{1/2} = 23$$

Thus we can say the amount of acetaminophen in the typical tablet in the batch of tablets is 446 mg with a sample standard deviation of 23 mg. Statistically this means that any additional measurement has a 68% probability (68 chances out of 100) of being between 423 mg ($446 - 23$) and 469 mg ($446 + 23$). Thus the standard deviation is a measure of the precision of a given type of determination.

The standard deviation gives us a means of describing the precision of a given type of determination using a series of replicate results. However, it is also useful to be able to estimate the precision of a procedure that involves several measurements by combining the precisions of the individual steps. That is, we want to answer

the following question: How do the uncertainties propagate when we combine the results of several different types of measurements? There are many ways to deal with the propagation of uncertainty. We will discuss only one simple method here.

A Simplified Method for Estimating Experimental Uncertainty

To illustrate this method, we will consider the determination of the density of an irregularly shaped solid. In this determination we make three measurements. First, we measure the mass of the object on a balance. Next, we must obtain the volume of the solid. The easiest method for doing this is to partially fill a graduated cylinder with a liquid and record the volume. Then we add the solid and record the volume again. The difference in the measured volumes is the volume of the solid. We can then calculate the density of the solid from the equation

$$D = \frac{M}{V_2 - V_1}$$

where M is the mass of the solid, V_1 is the initial volume of liquid in the graduated cylinder, and V_2 is the volume of liquid plus solid. Suppose we get the following results:

$$M = 23.06 \text{ g}$$

$$V_1 = 10.4 \text{ mL}$$

$$V_2 = 13.5 \text{ mL}$$

The calculated density is

$$\frac{23.06 \text{ g}}{13.5 \text{ mL} - 10.4 \text{ mL}} = 7.44 \text{ g/mL}$$

Now suppose that the precision of the balance used is $\pm 0.02 \text{ g}$ and that the volume measurements are precise to $\pm 0.05 \text{ mL}$. How do we estimate the uncertainty of the density? We can do this by assuming a worst case. That is, we assume the largest uncertainties in all measurements, and see what combinations of measurements will give the largest and smallest possible results (the greatest range). Since the density is the mass divided by the volume, the largest value of the density will be that obtained using the largest possible mass and the smallest possible volume:

$$D_{\max} = \frac{\overset{\text{Largest possible mass}}{\underset{\swarrow}{23.08}}}{\underset{\nearrow}{13.45} - \underset{\nwarrow}{10.45}} = 7.69 \text{ g/mL}$$

Smallest possible V_2 Largest possible V_1

The smallest value of the density is

$$D_{\min} = \frac{\underset{\text{Smallest possible mass}}{\underset{\swarrow}{23.04}}}{\underset{\nearrow}{13.35} - \underset{\nwarrow}{10.35}} = 7.20 \text{ g/mL}$$

Largest possible V_2 Smallest possible V_1

Thus the calculated range is from 7.20 to 7.69 and the average of these values is 7.44. The error limit is the number that gives the high and low range values when added and subtracted from the average. Therefore, we can express the density as $7.44 \pm 0.25 \text{ g/mL}$, which is the average value plus or minus the quantity that gives the range calculated by assuming the largest uncertainties.

Analysis of the propagation of uncertainties is useful in drawing qualitative conclusions from the analysis of measurements. For example, suppose that we obtained the above results for the density of an unknown alloy and we want to know if it is one of the following alloys:

$$\text{Alloy A: } D = 7.58 \text{ g/mL}$$

$$\text{Alloy B: } D = 7.42 \text{ g/mL}$$

$$\text{Alloy C: } D = 8.56 \text{ g/mL}$$

We can safely conclude that the alloy is not C. But the values of the densities for alloys A and B are both within the inherent uncertainty of our method. To distinguish between A and B, we need to improve the precision of our determination: The obvious choice is to improve the precision of the volume measurement.

The worst-case method is very useful in estimating uncertainties when the results of several measurements are combined to calculate a result. We assume the maximum uncertainty in each measurement and calculate the minimum and maximum possible result. These extreme values describe the range and thus the error limit.

Appendix Two The Quantitative Kinetic Molecular Model

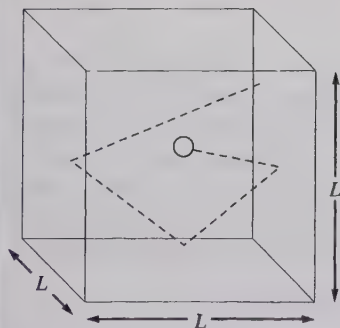


FIGURE A.3

An ideal gas particle in a cube whose sides are of length L . The particle collides elastically with the walls in a random, straightline motion.

We have seen that the kinetic molecular model successfully accounts for the properties of an ideal gas. This appendix will show in some detail how the postulates of the kinetic molecular model lead to an equation corresponding to the experimentally obtained ideal gas equation.

Recall that the particles of an ideal gas are assumed to be volumeless, to have no attraction for each other, and to produce pressure on their container by colliding with the container walls.

Suppose there are n moles of an ideal gas in a cubical container with sides each of length L . Assume each gas particle has a mass m and that it is in rapid, random, straight-line motion colliding with the walls, as shown in Fig. A.3. The collisions will be assumed to be *elastic*—no loss of kinetic energy occurs. We want to compute the force on the walls from the colliding gas particles and then, since pressure is force per unit area, to obtain an expression for the pressure of the gas.

Before we can derive the expression for the pressure of a gas, we must first discuss some characteristics of velocity. Each particle in the gas has a particular velocity u that can be divided into components u_x , u_y , and u_z , as shown in Fig. A.4. First, using u_x and u_y and the Pythagorean theorem, we can obtain u_{xy} as shown in Fig. A.4(c):

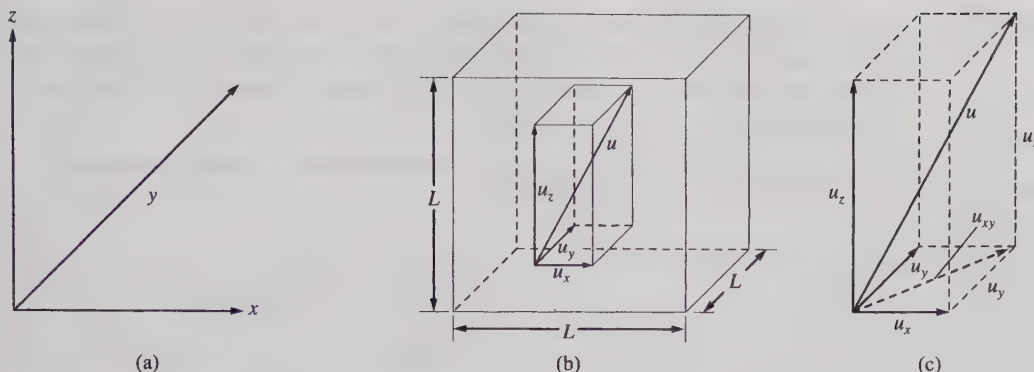
$$u_{xy}^2 = u_x^2 + u_y^2$$

$\nearrow$ Hypotenuse of right triangle $\nwarrow$ Sides of right triangle

Then, constructing another triangle as shown in Fig. A.4(c), we find

$$u^2 = u_{xy}^2 + u_z^2$$

$$\text{or } u^2 = u_x^2 + u_y^2 + u_z^2$$


FIGURE A.4

(a) The Cartesian coordinate axes.

(b) The velocity u of any gas particle can be broken down into three mutually perpendicular components, u_x , u_y , and u_z . This can be represented as a rectangular solid with sides u_x , u_y , and u_z and body diagonal u .

(c) In the xy plane,

$$u_x^2 + u_y^2 = u_{xy}^2$$

by the Pythagorean theorem. Since u_{xy} and u_x are also perpendicular,

$$u^2 = u_{xy}^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2$$

Now let's consider how an "average" gas particle moves. For example, how often does this particle strike the two walls of the box that are perpendicular to the x axis? It is important to realize that only the x component of the velocity affects the particle's impacts on these two walls, as shown in Fig. A.5(a). The larger the x component of the velocity, the faster the particle travels between these two walls, and the more impacts per unit of time it will make on these walls. Remember, the pressure of the gas is due to these collisions with the walls.

The collision frequency (collisions per unit of time) with the two walls that are perpendicular to the x axis is given by

$$\begin{aligned} (\text{Collision frequency})_x &= \frac{\text{velocity in the } x \text{ direction}}{\text{distance between the walls}} \\ &= \frac{u_x}{L} \end{aligned}$$

Next, what is the force of a collision? Force is defined as mass times acceleration (change in velocity per unit of time):

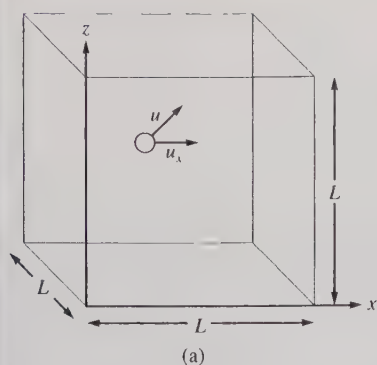
$$F = ma = m \left(\frac{\Delta u}{\Delta t} \right)$$

where F represents force, a represents acceleration, Δu represents a change in velocity, and Δt represents a given length of time.

Since we assume that the particle has constant mass, we can write

$$F = \frac{m \Delta u}{\Delta t} = \frac{\Delta(mu)}{\Delta t}$$

The quantity mu is the momentum of the particle (momentum is the product of mass and velocity), and the expression $F = \Delta(mu)/\Delta t$ implies that force is the change in momentum per unit of time. When a particle hits a wall perpendicular to the x axis, as shown in Fig. A.5(b), an elastic collision results in an *exact reversal* of the x component of velocity. That is, the *sign*, or direction, of u_x reverses when the particle



collides with one of the walls perpendicular to the x axis. Thus the final momentum is the *negative*, or opposite, of the initial momentum. Remember that an elastic collision means that there is no change in the *magnitude* of the velocity. The change in momentum in the x direction is then

$$\begin{aligned}\text{Change in momentum} &= \Delta(mu_x) = \text{final momentum} - \text{initial momentum} \\ &= -mu_x - mu_x \\ &\quad \uparrow \qquad \qquad \downarrow \\ &\quad \text{Final} \qquad \text{Initial} \\ &\quad \text{momentum} \quad \text{momentum} \\ &\quad \text{in } x \text{ direction} \quad \text{in } x \text{ direction} \\ &= -2mu_x\end{aligned}$$

But we are interested in the force the gas particle exerts on the walls of the box. Since we know that every action produces an equal but opposite reaction, the change in momentum with respect to the wall on impact is $-(-2mu_x)$, or $2mu_x$.

Recall that since force is the change in momentum per unit of time,

$$\text{Force}_x = \frac{\Delta(mu_x)}{\Delta t}$$

for the walls perpendicular to the x axis.

This expression can be obtained by multiplying the change in momentum per impact by the number of impacts per unit of time:

$$\text{Force}_x = (2mu_x) \left(\frac{u_x}{L} \right) = \text{change in momentum per impact} \times \text{Impacts per unit of time}$$

That is,

$$\text{Force}_x = \frac{2mu_x^2}{L}$$

So far we have considered only the two walls of the box perpendicular to the x axis. We can assume that the force on the two walls perpendicular to the y axis is given by

$$\text{Force}_y = \frac{2mu_y^2}{L}$$

and that on the two walls perpendicular to the z axis by

$$\text{Force}_z = \frac{2mu_z^2}{L}$$

Since we have shown that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

the total force on the box is

$$\begin{aligned}\text{Force}_{\text{TOTAL}} &= \text{force}_x + \text{force}_y + \text{force}_z \\ &= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L} \\ &= \frac{2m}{L}(u_x^2 + u_y^2 + u_z^2) = \frac{2m}{L}(u^2)\end{aligned}$$

FIGURE A.5

(a) Only the x component of the gas particle's velocity affects the frequency of impacts on the shaded walls, the walls that are perpendicular to the x axis. (b) For an elastic collision, there is an exact reversal of the x component of the velocity and of the total velocity. The change in momentum (final - initial) is then

$$-mu_x - mu_x = -2mu_x$$

Now since we want the average force, we use the average of the square of the velocity ($\overline{u^2}$) to obtain

$$\overline{\text{Force}}_{\text{TOTAL}} = \frac{2m}{L}(\overline{u^2})$$

Next, we need to compute the pressure (force per unit of area)

$$\begin{aligned} \text{Pressure due to "average" particle} &= \frac{\overline{\text{force}}_{\text{TOTAL}}}{\text{area}_{\text{TOTAL}}} \\ &= \frac{\frac{2m\overline{u^2}}{L}}{6L^2} = \frac{m\overline{u^2}}{3L^3} \end{aligned}$$

$\nearrow$ The 6 sides of the cube $\nwarrow$ Area of each side

Since the volume V of the cube is equal to L^3 , we can write

$$\text{Pressure} = P = \frac{m\overline{u^2}}{3V}$$

So far we have considered the pressure on the walls due to a single, "average" particle. Of course, we want the pressure due to the entire gas sample. The number of particles in a given gas sample can be expressed as follows:

$$\text{Number of gas particles} = nN_A$$

where n is the number of moles and N_A is Avogadro's number.

The total pressure on the box due to n moles of a gas is therefore

$$P = nN_A \frac{m\overline{u^2}}{3V}$$

Next we want to express the pressure in terms of the kinetic energy of the gas molecules. Kinetic energy (the energy due to motion) is given by $\frac{1}{2}mu^2$, where m is the mass and u is the velocity. Since we are using the average of the velocity squared ($\overline{u^2}$), and since $m\overline{u^2} = 2(\frac{1}{2}m\overline{u^2})$, we have

$$P = \left(\frac{2}{3}\right) \frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}$$

or

$$\frac{PV}{n} = \left(\frac{2}{3}\right) N_A(\frac{1}{2}m\overline{u^2})$$

Thus, based on the postulates of the kinetic molecular model, we have been able to derive an equation that has the same form as the ideal gas equation,

$$\frac{PV}{n} = RT$$

This agreement between experiment and theory supports the validity of the assumptions made in the kinetic molecular model about the behavior of gas particles, at least for the limiting case of an ideal gas.

Appendix Three Spectral Analysis

Although volumetric and gravimetric analyses are still very commonly used, spectroscopy is the technique most often used for modern chemical analysis. *Spectroscopy* is the study of electromagnetic radiation emitted or absorbed by a given chemical species. Since the quantity of radiation absorbed or emitted can be related to the quantity of the absorbing or emitting species present, this technique can be used for quantitative analysis. There are many spectroscopic techniques, as electromagnetic radiation spans a wide range of energies to include X rays, ultraviolet, infrared, and visible light, and microwaves, to name a few of its familiar forms. We will consider here only one procedure, which is based on the absorption of visible light.

If a liquid is colored, it is because some component of the liquid absorbs visible light. In a solution the greater the concentration of the light-absorbing substance, the more light absorbed, and the more intense the color of the solution.

The quantity of light absorbed by a substance can be measured by a *spectrophotometer*, shown schematically in Fig. A.6. This instrument consists of a source that emits all wavelengths of light in the visible region (wavelengths of ~ 400 to 700 nm); a monochromator, which selects a given wavelength of light; a sample holder for the solution being measured; and a detector, which compares the intensity of incident light I_0 to the intensity of light after it has passed through the sample I . The ratio I/I_0 , called the *transmittance*, is a measure of the fraction of light that passes through the sample. The amount of light absorbed is given by the *absorbance* A , where

$$A = -\log \frac{I}{I_0}$$

The absorbance can be expressed by the *Beer-Lambert law*:

$$A = \epsilon lc$$

where ϵ is the molar absorptivity or the molar extinction coefficient (in $\text{L/mol} \cdot \text{cm}$), l is the distance the light travels through the solution (in cm), and c is the concentration of the absorbing species (in mol/L). The Beer-Lambert law is the basis for using spectroscopy in quantitative analysis. If ϵ and l are known, measuring A for a solution allows us to calculate the concentration of the absorbing species in the solution.

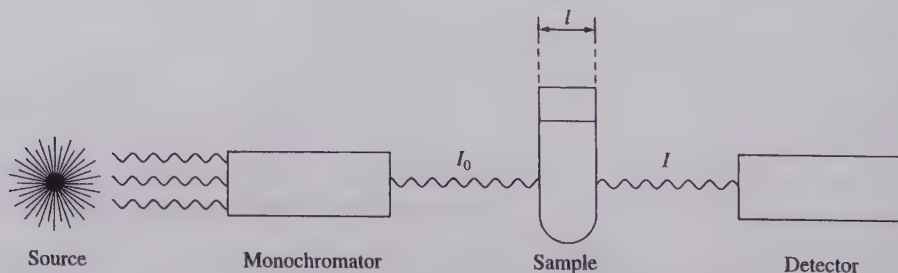


FIGURE A.6

A schematic diagram of a simple spectrophotometer. The source emits all wavelengths of visible light, which are dispersed using a prism or grating and then focused, one wavelength at a time, onto the sample. The detector compares the intensity of the incident light (I_0) to the intensity of the light after it has passed through the sample (I).

Suppose we have a pink solution containing an unknown concentration of $\text{Co}^{2+}(\text{aq})$ ions. A sample of this solution is placed in a spectrophotometer, and the absorbance is measured at a wavelength where ϵ for $\text{Co}^{2+}(\text{aq})$ is known to be $12 \text{ L/mol} \cdot \text{cm}$. The absorbance A is found to be 0.60. The width of the sample tube is 1.0 cm. We want to determine the concentration of $\text{Co}^{2+}(\text{aq})$ in the solution. This problem can be solved by a straightforward application of the Beer–Lambert law,

$$A = \epsilon l c$$

where

$$A = 0.60$$

$$\epsilon = \frac{12 \text{ L}}{\text{mol} \cdot \text{cm}}$$

$$l = \text{light path} = 1.0 \text{ cm}$$

Solving for the concentration gives

$$c = \frac{A}{\epsilon l} = \frac{0.60}{\left(12 \frac{\text{L}}{\text{mol} \cdot \text{cm}}\right)(1.0 \text{ cm})} = 5.0 \times 10^{-2} \text{ mol/L}$$

To obtain the unknown concentration of an absorbing species from the measured absorbance, we must know the product ϵl , since

$$c = \frac{A}{\epsilon l}$$

We can obtain the product ϵl by measuring the absorbance of a solution of *known* concentration, since

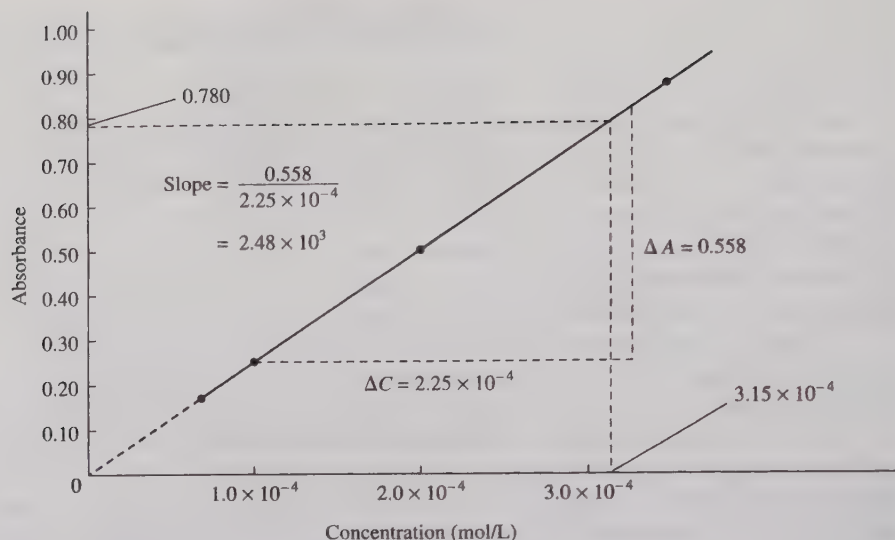
$$\epsilon l = \frac{A}{c}$$

↙ Measured using a spectrophotometer
 ↘ Known from making up the solution

However, a more accurate value of the product ϵl can be obtained by plotting A versus c for a series of solutions. Note that the equation $A = \epsilon l c$ gives a straight line with slope ϵl when A is plotted against c .

For example, consider the following typical spectroscopic analysis. A sample of steel from a bicycle frame is to be analyzed to determine its manganese content. The procedure involves weighing out a sample of the steel, dissolving it in strong acid, treating the resulting solution with a very strong oxidizing agent to convert all the manganese to permanganate ion (MnO_4^-), and then using spectroscopy to determine the concentration of the intensely purple MnO_4^- ions in the solution. To do this, however, the value of ϵl for MnO_4^- must be determined at an appropriate wavelength. The absorbance values for four solutions with known MnO_4^- concentrations were measured to give the following data:

Solution	Concentration of MnO_4^- (mol/L)	Absorbance
1	7.00×10^{-5}	0.175
2	1.00×10^{-4}	0.250
3	2.00×10^{-4}	0.500
4	3.50×10^{-4}	0.875

**FIGURE A.7**

A plot of absorbance versus concentration of MnO_4^- in a series of solutions of known concentration.

A plot of absorbance versus concentration for the solutions of known concentration is shown in Fig. A.7. The slope of this line (change in A /change in c) is $2.48 \times 10^3 \text{ L/mol}$. This quantity represents the product ϵl .

A sample of the steel weighing 0.1523 g was dissolved and the unknown amount of manganese was converted to MnO_4^- ions. Water was then added to give a solution with a final volume of 100.0 mL. A portion of this solution was placed in a spectrophotometer, and its absorbance was found to be 0.780. Using these data, we want to calculate the percent manganese in the steel. The MnO_4^- ions from the manganese in the dissolved steel sample show an absorbance of 0.780. Using the Beer-Lambert law, we calculate the concentration of MnO_4^- in this solution:

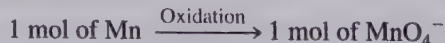
$$c = \frac{A}{\epsilon l} = \frac{0.780}{2.48 \times 10^3 \text{ L/mol}} \times 3.15 \times 10^{-4} \text{ mol/L}$$

There is a more direct way for finding c . Using a graph such as that in Fig. A.7 (often called a *Beer's law plot*), we can read the concentration that corresponds to $A = 0.780$. This interpolation is shown by dashed lines on the graph. By this method, $c = 3.15 \times 10^{-4} \text{ mol/L}$, which agrees with the value obtained above.

Recall that the original 0.1523-g steel sample was dissolved, the manganese was converted to permanganate, and the volume was adjusted to 100.0 mL. We now know that the $[\text{MnO}_4^-]$ in that solution is $3.15 \times 10^{-4} \text{ M}$. Using this concentration, we can calculate the total number of moles of MnO_4^- in that solution:

$$\begin{aligned} \text{mol of MnO}_4^- &= 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 3.15 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\ &= 3.15 \times 10^{-5} \text{ mol} \end{aligned}$$

Since each mole of manganese in the original steel sample yields a mole of MnO_4^- , that is,



the original steel sample must have contained $3.15 \times 10^{-5} \text{ mol}$ of manganese. The mass of manganese present in the sample is

$$3.15 \times 10^{-5} \text{ mol of Mn} \times \frac{54.938 \text{ g of Mn}}{1 \text{ mol of Mn}} = 1.73 \times 10^{-3} \text{ g of Mn}$$

Since the steel sample weighed 0.1523 g, the present manganese in the steel is

$$\frac{1.73 \times 10^{-3} \text{ g of Mn}}{1.523 \times 10^{-1} \text{ g of sample}} \times 100 = 1.14\%$$

This example illustrates a typical use of spectroscopy in quantitative analysis. The steps commonly involved are as follows:

1. Preparation of a calibration plot (a Beer's law plot) by measuring the absorbance values of a series of solutions with known concentrations.
2. Measurement of the absorbance of the solution of unknown concentration.
3. Use of the calibration plot to determine the unknown concentration.

Appendix Four Selected Thermodynamic Data

Note: All values are assumed precise to at least ± 1 .

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Aluminum			
Al(s)	0	0	28
Al ₂ O ₃ (s)	-1676	-1582	51
Al(OH) ₃ (s)	-1277		
AlCl ₃ (s)	-704	-629	111
Barium			
Ba(s)	0	0	67
BaCO ₃ (s)	-1219	-1139	112
BaO(s)	-582	-552	70
Ba(OH) ₂ (s)	-946		
BaSO ₄ (s)	-1465	-1353	132
Beryllium			
Be(s)	0	0	10
BeO(s)	-599	-569	14
Be(OH) ₂ (s)	-904	-815	47
Bromine			
Br ₂ (l)	0	0	152
Br ₂ (g)	31	3	245
Br ₂ (aq)	-3	4	130
Br ⁻ (aq)	-121	-104	82
HBr(g)	-36	-53	199
Cadmium			
Cd(s)	0	0	52
CdO(s)	-258	-228	55
Cd(OH) ₂ (s)	-561	-474	96
CdS(s)	-162	-156	65
CdSO ₄ (s)	-935	-823	123

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Calcium			
Ca(s)	0	0	41
CaC ₂ (s)	-63	-68	70
CaCO ₃ (s)	-1207	-1129	93
CaO(s)	-635	-604	40
Ca(OH) ₂ (s)	-987	-899	83
Ca ₃ (PO ₄) ₂ (s)	-4126	-3890	241
CaSO ₄ (s)	-1433	-1320	107
CaSiO ₃ (s)	-1630	-1550	84
Carbon			
C(s) (graphite)	0	0	6
C(s) (diamond)	2	3	2
CO(g)	-110.5	-137	198
CO ₂ (g)	-393.5	-394	214
CH ₄ (g)	-75	-51	186
CH ₃ OH(g)	-201	-163	240
CH ₃ OH(l)	-239	-166	127
H ₂ CO(g)	-116	-110	219
HCOOH(g)	-363	-351	249
HCN(g)	135.1	125	202
C ₂ H ₂ (g)	227	209	201
C ₂ H ₄ (g)	52	68	219
CH ₃ CHO(g)	-166	-129	250
C ₂ H ₅ OH(l)	-278	-175	161
C ₂ H ₆ (g)	-84.7	-32.9	229.5
C ₃ H ₆ (g)	20.9	62.7	266.9
C ₃ H ₈ (g)	-104	-24	270

(continued)

Appendix Four (continued)

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
<i>Carbon, continued</i>			
$C_2H_4O(g)$ (ethylene oxide)	-53	-13	242
$CH_2=CHCN(g)$	185.0	195.4	274
$CH_3COOH(l)$	-484	-389	160
$C_6H_{12}O_6(s)$	-1275	-911	212
CCl_4	-135	-65	216
<i>Chlorine</i>			
$Cl_2(g)$	0	0	223
$Cl_2(aq)$	-23	7	121
$Cl^-(aq)$	-167	-131	57
$HCl(g)$	-92	-95	187
<i>Chromium</i>			
$Cr(s)$	0	0	24
$Cr_2O_3(s)$	-1128	-1047	81
$CrO_3(s)$	-579	-502	72
<i>Copper</i>			
$Cu(s)$	0	0	33
$CuCO_3(s)$	-595	-518	88
$Cu_2O(s)$	-170	-148	93
$CuO(s)$	-156	-128	43
$Cu(OH)_2(s)$	-450	-372	108
$CuS(s)$	-49	-49	67
<i>Fluorine</i>			
$F_2(g)$	0	0	203
$F^-(aq)$	-333	-279	-14
$HF(g)$	-271	-273	174
<i>Hydrogen</i>			
$H_2(g)$	0	0	131
$H(g)$	217	203	115
$H^+(aq)$	0	0	0
$OH^-(aq)$	-230	-157	-11
$H_2O(l)$	-286	-237	70
$H_2O(g)$	-242	-229	189
<i>Iodine</i>			
$I_2(s)$	0	0	116
$I_2(g)$	62	19	261
$I_2(aq)$	23	16	137
$I^-(aq)$	-55	-52	106
<i>Iron</i>			
$Fe(s)$	0	0	27
$Fe_3C(s)$	21	15	108
$Fe_{0.95}O(s)$ (wustite)	-264	-240	59
FeO	-272	-255	61
$Fe_3O_4(s)$ (magnetite)	-1117	-1013	146
$Fe_2O_3(s)$ (hematite)	-826	-740	90
$FeS(s)$	-95	-97	67
$FeS_2(s)$	-178	-166	53
$FeSO_4(s)$	-929	-825	121

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
<i>Lead</i>			
$Pb(s)$	0	0	65
$PbO_2(s)$	-277	-217	69
$PbS(s)$	-100	-99	91
$PbSO_4(s)$	-920	-813	149
<i>Magnesium</i>			
$Mg(s)$	0	0	33
$MgCO_3(s)$	-1113	-1029	66
$MgO(s)$	-602	-569	27
$Mg(OH)_2(s)$	-925	-834	64
<i>Manganese</i>			
$Mn(s)$	0	0	32
$MnO(s)$	-385	-363	60
$Mn_3O_4(s)$	-1387	-1280	149
$Mn_2O_3(s)$	-971	-893	110
$MnO_2(s)$	-521	-466	53
$MnO_4^-(aq)$	-543	-449	190
<i>Mercury</i>			
$Hg(l)$	0	0	76
$Hg_2Cl_2(s)$	-265	-211	196
$HgCl_2(s)$	-230	-184	144
$HgO(s)$	-90	-59	70
$HgS(s)$	-58	-49	78
<i>Nickel</i>			
$Ni(s)$	0	0	30
$NiCl_2(s)$	-316	-272	107
$NiO(s)$	-241	-213	38
$Ni(OH)_2(s)$	-538	-453	79
$NiS(s)$	-93	-90	53
<i>Nitrogen</i>			
$N_2(g)$	0	0	192
$NH_3(g)$	-46	-17	193
$NH_3(aq)$	-80	-27	111
$NH_4^+(aq)$	-132	-79	113
$NO(g)$	90	87	211
$NO_2(g)$	34	52	240
$N_2O(g)$	82	104	220
$N_2O_4(g)$	10	98	304
$N_2O_4(l)$	-20	97	209
$N_2O_5(s)$	-42	134	178
$N_2H_4(l)$	51	149	121
$N_2H_3CH_3(l)$	54	180	166
$HNO_3(aq)$	-207	-111	146
$HNO_3(l)$	-174	-81	156
$NH_4ClO_4(s)$	-295	-89	186
$NH_4Cl(s)$	-314	-203	96
<i>Oxygen</i>			
$O_2(g)$	0	0	205
$O(g)$	249	232	161
$O_3(g)$	143	163	239

Appendix Four (continued)

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Phosphorus			
P(s) (white)	0	0	41
P(s) (red)	-18	-12	23
P(s) (black)	-39	-33	23
P ₄ (g)	59	24	280
PF ₃ (g)	-1578	-1509	296
PH ₃ (g)	5	13	210
H ₃ PO ₄ (s)	-1279	-1119	110
H ₃ PO ₄ (l)	-1267	—	—
H ₃ PO ₄ (aq)	-1288	-1143	158
P ₄ O ₁₀ (s)	-2984	-2698	229
Potassium			
K(s)	0	0	64
KCl(s)	-436	-408	83
KClO ₃ (s)	-391	-290	143
KClO ₄ (s)	-433	-304	151
K ₂ O(s)	-361	-322	98
K ₂ O ₂ (s)	-496	-430	113
KO ₂ (s)	-283	-238	117
KOH(s)	-425	-379	79
KOH(aq)	-481	-440	9.20
Silicon			
SiO ₂ (s) (quartz)	-911	-856	42
SiCl ₄ (l)	-687	-620	240
Silver			
Ag(s)	0	0	43
Ag ⁺ (aq)	105	77	73
AgBr(s)	-100	-97	107
AgCN(s)	146	164	84
AgCl(s)	-127	-110	96
Ag ₂ CrO ₄ (s)	-712	-622	217
AgI(s)	-62	-66	115
Ag ₂ O(s)	-31	-11	122
Ag ₂ S(s)	-32	-40	146
Sodium			
Na(s)	0	0	51
Na ⁺ (aq)	-240	-262	59
NaBr(s)	-360	-347	84
Na ₂ CO ₃ (s)	-1131	-1048	136
NaHCO ₃ (s)	-948	-852	102
NaCl(s)	-411	-384	72
NaH(s)	-56	-33	40
NaI(s)	-288	-282	91
NaNO ₂ (s)	-359	—	—
NaNO ₃ (s)	-467	-366	116

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Sodium, <i>continued</i>			
Na ₂ O(s)	-416	-377	73
Na ₂ O ₂ (s)	-515	-451	95
NaOH(s)	-427	-381	64
NaOH(aq)	-470	-419	50
Sulfur			
S(s) (rhombic)	0	0	32
S(s) (monoclinic)	0.3	0.1	33
S ²⁻ (aq)	33	86	-15
S ₈ (g)	102	50	431
SF ₆ (g)	-1209	-1105	292
H ₂ S(g)	-21	-34	206
SO ₂ (g)	-297	-300	248
SO ₃ (g)	-396	-371	257
SO ₄ ²⁻ (aq)	-909	-745	20
H ₂ SO ₄ (l)	-814	-690	157
H ₂ SO ₄ (aq)	-909	-745	20
Tin			
Sn(s) (white)	0	0	52
Sn(s) (gray)	-2	0.1	44
SnO(s)	-285	-257	56
SnO ₂ (s)	-581	-520	52
Sn(OH) ₂ (s)	-561	-492	155
Titanium			
TiCl ₄ (g)	-763	-727	355
TiO ₂ (s)	-945	-890	50
Uranium			
U(s)	0	0	50
UF ₆ (s)	-2137	-2008	228
UF ₆ (g)	-2113	-2029	380
UO ₂ (s)	-1084	-1029	78
U ₃ O ₈ (s)	-3575	-3393	282
UO ₃ (s)	-1230	-1150	99
Xenon			
Xe(g)	0	0	170
XeF ₂ (g)	-108	-48	254
XeF ₄ (s)	-251	-121	146
XeF ₆ (g)	-294	—	—
XeO ₃ (s)	402	—	—
Zinc			
Zn(s)	0	0	42
ZnO(s)	-348	-318	44
Zn(OH) ₂ (s)	-642	—	—
ZnS(s) (wurtzite)	-193	—	—
ZnS(s) (zinc blende)	-206	-201	58
ZnSO ₄ (s)	-983	-874	120

Appendix Five Equilibrium Constants and Reduction Potentials

A5.1 Values of K_a for Some Common Monoprotic Acids

Name	Formula	Value of K_a
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}
Chlorous acid	HClO_2	1.2×10^{-2}
Monochloroacetic acid	$\text{HC}_2\text{H}_2\text{ClO}_2$	1.35×10^{-3}
Hydrofluoric acid	HF	7.2×10^{-4}
Nitrous acid	HNO_2	4.0×10^{-4}
Formic acid	HCO_2H	1.8×10^{-4}
Lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	1.38×10^{-4}
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.4×10^{-5}
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
Hydrated aluminum(III) ion	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	1.4×10^{-5}
Propanoic acid	$\text{HC}_3\text{H}_5\text{O}_2$	1.3×10^{-5}
Hypochlorous acid	HOCl	3.5×10^{-8}
Hypobromous acid	HOBr	2×10^{-9}
Hydrocyanic acid	HCN	6.2×10^{-10}
Boric acid	H_3BO_3	5.8×10^{-10}
Ammonium ion	NH_4^+	5.6×10^{-10}
Phenol	HOC_6H_5	1.6×10^{-10}
Hypoiodous acid	HOI	2×10^{-11}

A5.2 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	
Citric acid	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	8.4×10^{-4}	1.8×10^{-5}	4.0×10^{-6}

A5.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	CH_3NH_3^+	4.38×10^{-4}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	5.6×10^{-4}
Diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH}$	$(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	1.3×10^{-3}
Triethylamine	$(\text{C}_2\text{H}_5)_3\text{N}$	$(\text{C}_2\text{H}_5)_3\text{NH}^+$	4.0×10^{-4}
Hydroxylamine	HONH_2	HONH_3^+	1.1×10^{-8}
Hydrazine	H_2NNH_2	H_2NNH_3^+	3.0×10^{-6}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	3.8×10^{-10}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}

A5.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		$\text{Hg}_2\text{CrO}_4^*$	2×10^{-9}	$\text{Co}(\text{OH})_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	BaCrO_4	8.5×10^{-11}	$\text{Ni}(\text{OH})_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$\text{Zn}(\text{OH})_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	PbCrO_4	2×10^{-16}	$\text{Cu}(\text{OH})_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$\text{Hg}(\text{OH})_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	Carbonates		$\text{Sn}(\text{OH})_2$	3×10^{-27}
Chlorides		NiCO_3	1.4×10^{-7}	$\text{Cr}(\text{OH})_3$	6.7×10^{-31}
PbCl_2	1.6×10^{-5}	CaCO_3	8.7×10^{-9}	$\text{Al}(\text{OH})_3$	2×10^{-32}
AgCl	1.6×10^{-10}	BaCO_3	1.6×10^{-9}	$\text{Fe}(\text{OH})_3$	4×10^{-38}
Hg_2Cl_2^*	1.1×10^{-18}	SrCO_3	7×10^{-10}	$\text{Co}(\text{OH})_3$	2.5×10^{-43}
Bromides		CuCO_3	2.5×10^{-10}	Sulfides	
PbBr_2	4.6×10^{-6}	ZnCO_3	2×10^{-10}	MnS	2.3×10^{-13}
AgBr	5.0×10^{-13}	MnCO_3	8.8×10^{-11}	FeS	3.7×10^{-19}
Hg_2Br_2^*	1.3×10^{-22}	FeCO_3	2.1×10^{-11}	NiS	3×10^{-21}
Iodides		Ag_2CO_3	8.1×10^{-12}	CoS	5×10^{-22}
PbI_2	1.4×10^{-8}	CdCO_3	5.2×10^{-12}	ZnS	2.5×10^{-22}
AgI	1.5×10^{-16}	PbCO_3	1.5×10^{-15}	SnS	1×10^{-26}
Hg_2I_2^*	4.5×10^{-29}	MgCO_3	1×10^{-5}	CdS	1.0×10^{-28}
Sulfates		Hg_2CO_3^*	9.0×10^{-15}	PbS	7×10^{-29}
CaSO_4	6.1×10^{-5}	Hydroxides		CuS	8.5×10^{-45}
Ag_2SO_4	1.2×10^{-5}	$\text{Ba}(\text{OH})_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
SrSO_4	3.2×10^{-7}	$\text{Sr}(\text{OH})_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
PbSO_4	1.3×10^{-8}	$\text{Ca}(\text{OH})_2$	1.3×10^{-6}	Phosphates	
BaSO_4	1.5×10^{-9}	AgOH	2.0×10^{-8}	Ag_3PO_4	1.8×10^{-18}
Chromates		$\text{Mg}(\text{OH})_2$	8.9×10^{-12}	$\text{Sr}_3(\text{PO}_4)_2$	1×10^{-31}
SrCrO_4	3.6×10^{-5}	$\text{Mn}(\text{OH})_2$	2×10^{-13}	$\text{Ca}_3(\text{PO}_4)_2$	1.3×10^{-32}
		$\text{Cd}(\text{OH})_2$	5.9×10^{-15}	$\text{Ba}_3(\text{PO}_4)_2$	6×10^{-39}
		$\text{Pb}(\text{OH})_2$	1.2×10^{-15}	$\text{Pb}_3(\text{PO}_4)_2$	1×10^{-54}
		$\text{Fe}(\text{OH})_2$	1.8×10^{-15}		

*Contains Hg_2^{2+} ions. $K_{sp} = [\text{Hg}_2^{2+}][\text{X}^-]^2$ for Hg_2X_2 salts.

A5.5 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathcal{E}^\circ$ (V)	Half-Reaction	$\mathcal{E}^\circ$ (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.34
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$2\text{e}^- + 2\text{H}^+ + \text{IO}_4^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

Appendix Six SI Units and Conversion Factors

Length

SI unit: meter (m)

1 meter	= 1.0936 yards
1 centimeter	= 0.39370 inch
1 inch	= 2.54 centimeters (exactly)
1 kilometer	= 0.62137 mile
1 mile	= 5280 feet = 1.6093 kilometers
1 angstrom	= 10^{-10} meter = 100 picometers

Mass

SI unit: kilogram (kg)

1 kilogram	= 1000 grams = 2.2046 pounds
1 pound	= 453.59 grams = 0.45359 kilogram = 16 ounces
1 ton	= 2000 pounds = 907.185 kilograms
1 metric ton	= 1000 kilograms = 2204.6 pounds
1 atomic mass unit	= 1.66056×10^{-27} kilograms

Volume

SI unit: cubic meter (m³)

1 liter	= 10^{-3} m ³ = 1 dm ³ = 1.0567 quarts
1 gallon	= 4 quarts = 8 pints = 3.7854 liters
1 quart	= 32 fluid ounces = 0.94633 liter

Temperature

SI unit: kelvin (K)

0 K	= -273.15°C = -459.67°F
K	= °C + 273.15
°C	= $\frac{5}{9}(\text{°F} - 32)$
°F	= $\frac{9}{5}(\text{°C}) + 32$

Energy

SI unit: joule (J)

1 joule	= 1 kg · m ² /s ² = 0.23901 calorie = 9.4781×10^{-4} btu (British thermal unit)
1 calorie	= 4.184 joules = 3.965×10^{-3} btu
1 btu	= 1055.06 joules = 252.2 calories

Pressure

SI unit: pascal (Pa)

1 pascal	= 1 N/m ² = 1 kg/m · s ²
1 atmosphere	= 101.325 kilopascals = 760 torr (mmHg) = 14.70 pounds per square inch
1 bar	= 10^5 pascals



Glossary

- Accuracy** the agreement of a particular value with the true value. (1.4)
- Acid** a substance that produces hydrogen ions in solution; a proton donor. (2.8; 4.2; 4.8)
- Acid-base indicator** a substance that marks the end point of an acid-base titration by changing color. (15.5)
- Acid dissociation constant (K_a)** the equilibrium constant for a reaction in which a proton is removed from an acid by H_2O to form the conjugate base and H_3O^+ . (14.1)
- Acid rain** a result of air pollution by sulfur dioxide. (5.9)
- Acidic oxide** a covalent oxide that dissolves in water to give an acidic solution. (14.10)
- Actinide series** a group of 14 elements following actinium in the periodic table, in which the $5f$ orbitals are being filled. (7.11; 19.1)
- Activated complex (transition state)** the arrangement of atoms found at the top of the potential energy barrier as a reaction proceeds from reactants to products. (12.7)
- Activation energy** the threshold energy that must be overcome to produce a chemical reaction. (12.7)
- Addition polymerization** a type of polymerization in which the monomers simply add together to form the polymer, with no other products. (22.5)
- Addition reaction** a reaction in which atoms add to a carbon-carbon multiple bond. (22.2)
- Adsorption** the collection of one substance on the surface of another. (12.8)
- Air pollution** contamination of the atmosphere, mainly by the gaseous products of transportation and production of electricity. (5.9)
- Alcohol** an organic compound in which the hydroxyl group is a substituent on a hydrocarbon. (22.4)
- Aldehyde** an organic compound containing the carbonyl group bonded to at least one hydrogen atom. (22.4)
- Alkali metal** a Group 1A metal. (2.7; 19.2)
- Alkaline earth metal** a Group 2A metal. (2.7; 19.4)
- Alkane** a saturated hydrocarbon with the general formula C_nH_{2n+2} . (22.1)
- Alkene** an unsaturated hydrocarbon containing a carbon-carbon double bond. The general formula is C_nH_{2n} . (22.2)
- Alkyne** an unsaturated hydrocarbon containing a triple carbon-carbon bond. The general formula is C_nH_{2n-2} . (22.2)
- Alloy** a substance that contains a mixture of elements and has metallic properties. (10.4)
- Alloy steel** a form of steel containing carbon plus other metals such as chromium, cobalt, manganese, and molybdenum. (21.8)
- Alpha (α) particle** a helium nucleus. (18.1)
- Alpha-particle production** a common mode of decay for radioactive nuclides in which the mass number changes. (18.1)
- Amine** an organic base derived from ammonia in which one or more of the hydrogen atoms are replaced by organic groups. (14.6; 22.4)
- α -Amino acid** an organic acid in which an amino group and an R group are attached to the carbon atom next to the carboxyl group. (22.6)
- Amorphous solid** a solid with considerable disorder in its structure. (10.3)
- Ampere** the unit of electric current equal to one coulomb of charge per second. (17.7)
- Amphoteric substance** a substance that can behave either as an acid or as a base. (14.2)
- Angular momentum quantum number (ℓ)** the quantum number relating to the shape of an atomic orbital, which can assume any integral value from 0 to $n - 1$ for each value of n . (7.6)
- Anion** a negative ion. (2.6)
- Anode** the electrode in a galvanic cell at which oxidation occurs. (17.1)
- Antibonding molecular orbital** an orbital higher in energy than the atomic orbitals of which it is composed. (9.2)
- Aqueous solution** a solution in which water is the dissolving medium or solvent. (4)
- Aromatic hydrocarbon** one of a special class of cyclic unsaturated hydrocarbons, the simplest of which is benzene. (22.3)
- Arrhenius concept** a concept postulating that acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions. (14.1)
- Arrhenius equation** the equation representing the rate constant as $k = Ae^{-E_a/RT}$, where A represents the product of the collision frequency and the steric factor, and $e^{-E_a/RT}$ is the fraction of collisions with sufficient energy to produce a reaction. (12.7)
- Atactic chain** a polymer chain in which the substituent groups such as CH_3 are randomly distributed along the chain. (22.5)
- Atmosphere** the mixture of gases that surrounds the earth's surface. (5.9)
- Atomic number** the number of protons in the nucleus of an atom. (2.5; 18)
- Atomic radius** half the distance between the nuclei in a molecule consisting of identical atoms. (7.12)
- Atomic solid** a solid that contains atoms at the lattice points. (10.3)
- Atomic weight** the weighted average mass of the atoms in a naturally occurring element. (2.3)
- Aufbau principle** the principle stating that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen-like orbitals. (7.11)
- Autoionization** the transfer of a proton from one molecule to another of the same substance. (14.2)
- Avogadro's law** equal volumes of gases at the same temperature and pressure contain the same number of particles. (5.2)

- Avogadro's number** the number of atoms in exactly 12 grams of pure ^{12}C , equal to 6.022×10^{23} . (3.2)
- Ball-and-stick model** a molecular model that distorts the sizes of atoms but shows bond relationships clearly. (2.6)
- Band model** a molecular model for metals in which the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms. (10.4)
- Barometer** a device for measuring atmospheric pressure. (5.1)
- Base** a substance that produces hydroxide ions in aqueous solution, a proton acceptor. (4.8)
- Basic oxide** an ionic oxide that dissolves in water to produce a basic solution. (14.10)
- Basic oxygen process** a process for producing steel by oxidizing and removing the impurities in iron using a high-pressure blast of oxygen. (21.8)
- Battery** a group of galvanic cells connected in series. (17.5)
- Beta (β) particle** an electron produced in radioactive decay. (18.1)
- Beta-particle production** a decay process for radioactive nuclides in which the mass number remains constant and the atomic number changes. The net effect is to change a neutron to a proton. (18.1)
- Bidentate ligand** a ligand that can form two bonds to a metal ion. (21.3)
- Bimolecular step** a reaction involving the collision of two molecules. (12.6)
- Binary compound** a two-element compound. (2.8)
- Binding energy (nuclear)** the energy required to decompose a nucleus into its component nucleons. (18.5)
- Biomolecule** a molecule responsible for maintaining and/or reproducing life. (22)
- Blast furnace** a furnace in which iron oxide is reduced to iron metal by using a very strong blast of hot air to produce carbon monoxide from coke, and then using this gas as a reducing agent for the iron. (21.8)
- Bond energy** the energy required to break a given chemical bond. (8.1)
- Bond length** the distance between the nuclei of the two atoms connected by a bond; the distance where the total energy of a diatomic molecule is minimal. (8.1)
- Bond order** the difference between the number of bonding electrons and the number of antibonding electrons, divided by two. It is an index of bond strength. (9.2)
- Bonding molecular orbital** an orbital lower in energy than the atomic orbitals of which it is composed. (9.2)
- Bonding pair** an electron pair found in the space between two atoms. (8.9)
- Borane** a covalent hydride of boron. (19.5)
- Boyle's law** the volume of a given sample of gas at constant temperature varies inversely with the pressure. (5.2)
- Breeder reactor** a nuclear reactor in which fissionable fuel is produced while the reactor runs. (18.6)
- Brønsted-Lowry model** a model proposing that an acid is a proton donor, and a base is a proton acceptor. (14.1)
- Buffered solution** a solution that resists a change in its pH when either hydroxide ions or protons are added. (15.2)
- Buffering capacity** the ability of a buffered solution to absorb protons or hydroxide ions without a significant change in pH; determined by the magnitudes of $[\text{HA}]$ and $[\text{A}^-]$ in the solution. (15.3)
- Calorimetry** the science of measuring heat flow. (6.2)
- Capillary action** the spontaneous rising of a liquid in a narrow tube. (10.2)
- Carbohydrate** a polyhydroxyl ketone or polyhydroxyl aldehyde or a polymer composed of these. (22.6)
- Carbon steel** an alloy of iron containing up to about 1.5% carbon. (21.8)
- Carboxyhemoglobin** a stable complex of hemoglobin and carbon monoxide that prevents normal oxygen uptake in the blood. (21.7)
- Carboxyl group** the $-\text{COOH}$ group in an organic acid. (14.2; 22.4)
- Carboxylic acid** an organic compound containing the carboxyl group; an acid with the general formula RCOOH . (22.4)
- Catalyst** a substance that speeds up a reaction without being consumed. (12.8)
- Cathode** the electrode in a galvanic cell at which reduction occurs. (17.1)
- Cathode rays** the "rays" emanating from the negative electrode (cathode) in a partially evacuated tube; a stream of electrons. (2.4)
- Cathodic protection** a method in which an active metal, such as magnesium, is connected to steel to protect it from corrosion. (17.6)
- Cation** a positive ion. (2.6)
- Cell potential (electromotive force)** the driving force in a galvanic cell that pulls electrons from the reducing agent in one compartment to the oxidizing agent in the other. (17.1)
- Ceramic** a nonmetallic material made from clay and hardened by firing at high temperature; it contains minute silicate crystals suspended in a glassy cement. (10.5)
- Chain reaction (nuclear)** a self-sustaining fission process caused by the production of neutrons that proceed to split other nuclei. (18.6)
- Charles's law** the volume of a given sample of gas at constant pressure is directly proportional to the temperature in kelvins. (5.2)
- Chelating ligand (chelate)** a ligand having more than one atom with a lone pair that can be used to bond to a metal ion. (21.3)
- Chemical bond** the force or, more accurately, the energy, that holds two atoms together in a compound. (2.6)
- Chemical change** the change of substances into other substances through a reorganization of the atoms; a chemical reaction. (1.9)
- Chemical equation** a representation of a chemical reaction showing the relative numbers of reactant and product molecules. (3.6)
- Chemical equilibrium** a dynamic reaction system in which the concentrations of all reactants and products remain constant as a function of time. (13)

- Chemical formula** the representation of a molecule in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to show the relative numbers of atoms. (2.6)
- Chemical kinetics** the area of chemistry that concerns reaction rates. (12)
- Chemical stoichiometry** the calculation of the quantities of material consumed and produced in chemical reactions. (3)
- Chirality** the quality of having nonsuperimposable mirror images. (21.4)
- Chlor-alkali process** the process for producing chlorine and sodium hydroxide by electrolyzing brine in a mercury cell. (17.8)
- Chromatography** the general name for a series of methods for separating mixtures by employing a system with a mobile phase and a stationary phase. (1.9)
- Coagulation** the destruction of a colloid by causing particles to aggregate and settle out. (11.8)
- Codons** organic bases in sets of three that form the genetic code. (22.6)
- Colligative properties** properties of a solution that depend only on the number, and not on the identity, of the solute particles. (11.5)
- Collision model** a model based on the idea that molecules must collide to react; used to account for the observed characteristics of reaction rates. (12.7)
- Colloid (colloidal dispersion)** a suspension of particles in a dispersing medium. (11.8)
- Combustion reaction** the vigorous and exothermic reaction that takes place between certain substances, particularly organic compounds, and oxygen. (22.1)
- Common ion effect** the shift in an equilibrium position caused by the addition or presence of an ion involved in the equilibrium reaction. (15.1)
- Complete ionic equation** an equation that shows all substances that are strong electrolytes as ions. (4.6)
- Complex ion** a charged species consisting of a metal ion surrounded by ligands. (15.8; 21.1)
- Compound** a substance with constant composition that can be broken down into elements by chemical processes. (1.9)
- Concentration cell** a galvanic cell in which both compartments contain the same components, but at different concentrations. (17.4)
- Condensation** the process by which vapor molecules reform a liquid. (10.8)
- Condensation polymerization** a type of polymerization in which the formation of a small molecule, such as water, accompanies the extension of the polymer chain. (22.5)
- Condensation reaction** a reaction in which two molecules are joined, accompanied by the elimination of a water molecule. (20.3)
- Condensed states of matter** liquids and solids. (10.1)
- Conjugate acid** the species formed when a proton is added to a base. (14.1)
- Conjugate acid-base pair** two species related to each other by the donating and accepting of a single proton. (14.1)
- Conjugate base** what remains of an acid molecule after a proton is lost. (14.1)
- Continuous spectrum** a spectrum that exhibits all the wavelengths of visible light. (7.3)
- Control rods** rods in a nuclear reactor composed of substances that absorb neutrons. These rods regulate the power level of the reactor. (18.6)
- Coordinate covalent bond** a metal-ligand bond resulting from the interaction of a Lewis base (the ligand) and a Lewis acid (the metal ion). (21.3)
- Coordination compound** a compound composed of a complex ion and counter ions sufficient to give no net charge. (21.3)
- Coordination isomerism** isomerism in a coordination compound in which the composition of the coordination sphere of the metal ion varies. (21.4)
- Coordination number** the number of bonds formed between the metal ion and the ligands in a complex ion. (21.3)
- Copolymer** a polymer formed from the polymerization of more than one type of monomer. (22.5)
- Core electron** an inner electron in an atom; one not in the outermost (valence) principal quantum level. (7.11)
- Corrosion** the process by which metals are oxidized in the atmosphere. (17.6)
- Coulomb's law** $E = 2.31 \times 10^{-19} \left(\frac{Q_1 Q_2}{r} \right)$, where E is the energy of interaction between a pair of ions, expressed in joules; r is the distance between the ion centers in nm; and Q_1 and Q_2 are the numerical ion charges. (8.1)
- Counterions** anions or cations that balance the charge on the complex ion in a coordination compound. (21.3)
- Covalent bonding** a type of bonding in which electrons are shared by atoms. (2.6; 8.1)
- Critical mass** the mass of fissionable material required to produce a self-sustaining chain reaction. (18.6)
- Critical point** the point on a phase diagram at which the temperature and pressure have their critical values; the end point of the liquid-vapor line. (10.9)
- Critical pressure** the minimum pressure required to produce liquefaction of a substance at the critical temperature. (10.9)
- Critical reaction (nuclear)** a reaction in which exactly one neutron from each fission event causes another fission event, thus sustaining the chain reaction. (18.6)
- Critical temperature** the temperature above which vapor cannot be liquefied no matter what pressure is applied. (10.9)
- Crosslinking** the existence of bonds between adjacent chains in a polymer, thus adding strength to the material. (22.5)
- Crystal field model** a model used to explain the magnetism and colors of coordination complexes through the splitting of the d orbital energies. (21.6)
- Crystalline solid** a solid with a regular arrangement of its components. (10.3)
- Cubic closest packed (ccp) structure** a solid modeled by the closest packing of spheres with an $abcabc$ arrangement of layers; the unit cell is face-centered cubic. (10.4)
- Cyanidation** a process in which crushed gold ore is treated with an aqueous cyanide solution in the presence of air to dissolve the gold. Pure gold is recovered by reduction of the ion to the metal. (21.8)
- Cyclotron** a type of particle accelerator in which an ion introduced at the center is accelerated in an expanding spiral path by the

- use of alternating electrical fields in the presence of a magnetic field. (18.3)
- Cytochromes** a series of iron-containing species composed of heme and a protein. Cytochromes are the principal electron-transfer molecules in the respiratory chain. (21.7)
- Dalton's law of partial pressures** for a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone. (5.5)
- Degenerate orbitals** a group of orbitals with the same energy. (7.7)
- Dehydrogenation reaction** a reaction in which two hydrogen atoms are removed from adjacent carbons of a saturated hydrocarbon, giving an unsaturated hydrocarbon. (22.1)
- Denaturation** the breaking down of the three-dimensional structure of a protein resulting in the loss of its function. (22.6)
- Denitrification** the return of nitrogen from decomposed matter to the atmosphere by bacteria that change nitrates to nitrogen gas. (20.2)
- Density** a property of matter representing the mass per unit volume. (1.8)
- Deoxyribonucleic acid (DNA)** a huge nucleotide polymer having a double-helical structure with complementary bases on the two strands. Its major functions are protein synthesis and the storage and transport of genetic information. (22.6)
- Desalination** the removal of dissolved salts from an aqueous solution. (11.6)
- Dialysis** a phenomenon in which a semipermeable membrane allows transfer of both solvent molecules and small solute molecules and ions. (11.6)
- Diamagnetism** a type of magnetism, associated with paired electrons, that causes a substance to be repelled from the inducing magnetic field. (9.3)
- Differential rate law** an expression that gives the rate of a reaction as a function of concentrations; often called the rate law. (12.2)
- Diffraction** the scattering of light from a regular array of points or lines, producing constructive and destructive interference. (7.2)
- Diffusion** the mixing of gases. (5.7)
- Dilution** the process of adding solvent to lower the concentration of solute in a solution. (4.3)
- Dimer** a molecule formed by the joining of two identical monomers. (22.5)
- Dipole-dipole attraction** the attractive force resulting when polar molecules line up so that the positive and negative ends are close to each other. (10.1)
- Dipole moment** a property of a molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge. (8.3)
- Direct reduction furnace** a furnace in which iron oxide is reduced to iron metal using milder reaction conditions than in a blast furnace. (21.8)
- Disaccharide** a sugar formed from two monosaccharides joined by a glycoside linkage. (22.6)
- Disproportionation reaction** a reaction in which a given element is both oxidized and reduced. (20.7)
- Distillation** a method for separating the components of a liquid mixture that depends on differences in the ease of vaporization of the components. (1.9)
- Disulfide linkage** an S—S bond that stabilizes the tertiary structure of many proteins. (22.6)
- Double bond** a bond in which two pairs of electrons are shared by two atoms. (8.8)
- Downs cell** a cell used for electrolyzing molten sodium chloride. (17.8)
- Dry cell battery** a common battery used in calculators, watches, radios, and tape players. (17.5)
- Dual nature of light** the statement that light exhibits both wave and particulate properties. (7.2)
- Effusion** the passage of a gas through a tiny orifice into an evacuated chamber. (5.7)
- Electrical conductivity** the ability to conduct an electric current. (4.2)
- Electrochemistry** the study of the interchange of chemical and electrical energy. (17)
- Electrolysis** a process that involves forcing a current through a cell to cause a nonspontaneous chemical reaction to occur. (17.7)
- Electrolyte** a material that dissolves in water to give a solution that conducts an electric current. (4.2)
- Electrolytic cell** a cell that uses electrical energy to produce a chemical change that would otherwise not occur spontaneously. (17.7)
- Electromagnetic radiation** radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum. (7.1)
- Electron** a negatively charged particle that moves around the nucleus of an atom. (2.4)
- Electron affinity** the energy change associated with the addition of an electron to a gaseous atom. (7.12)
- Electron capture** a process in which one of the inner-orbital electrons in an atom is captured by the nucleus. (18.1)
- Electron spin quantum number** a quantum number representing one of the two possible values for the electron spin; either $+\frac{1}{2}$ or $-\frac{1}{2}$. (7.8)
- Electronegativity** the tendency of an atom in a molecule to attract shared electrons to itself. (8.2)
- Element** a substance that cannot be decomposed into simpler substances by chemical or physical means. (1.9)
- Elementary step** a reaction whose rate law can be written from its molecularity. (12.6)
- $E = mc^2$** Einstein's equation proposing that energy has mass; E is energy, m is mass, and c is the speed of light. (7.2)
- Empirical formula** the simplest whole number ratio of atoms in a compound. (3.5)
- Enantiomers** isomers that are nonsuperimposable mirror images of each other. (21.4)
- Endpoint** the point in a titration at which the indicator changes color. (4.8)

- Endothermic** refers to a reaction where energy (as heat) flows into the system. (6.1)
- Energy** the capacity to do work or to cause heat flow. (6.1)
- Enthalpy** a property of a system equal to $E + PV$, where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system. At constant pressure the change in enthalpy equals the energy flow as heat. (6.2)
- Enthalpy (heat) of fusion** the enthalpy change that occurs to melt a solid at its melting point. (10.8)
- Entropy** a thermodynamic function that measures randomness or disorder. (16.1)
- Enzyme** a large molecule, usually a protein, that catalyzes biological reactions. (12.8)
- Equilibrium constant** the value obtained when equilibrium concentrations of the chemical species are substituted in the equilibrium expression. (13.2)
- Equilibrium expression** the expression (from the law of mass action) obtained by multiplying the product concentrations and dividing by the multiplied reactant concentrations, with each concentration raised to a power represented by the coefficient in the balanced equation. (13.2)
- Equilibrium point (thermodynamic definition)** the position where the free energy of a reaction system has its lowest possible value. (16.8)
- Equilibrium position** a particular set of equilibrium concentrations. (13.2)
- Equivalence point (stoichiometric point)** the point in a titration when enough titrant has been added to react exactly with the substance in solution being titrated. (4.9; 15.4)
- Ester** an organic compound produced by the reaction between a carboxylic acid and an alcohol. (22.4)
- Exothermic** refers to a reaction where energy (as heat) flows out of the system. (6.1)
- Exponential notation** expresses a number as $N \times 10^M$, a convenient method for representing a very large or very small number and for easily indicating the number of significant figures. (1.5)
- Faraday** a constant representing the charge on one mole of electrons; 96,485 coulombs. (17.3)
- Filtration** a method for separating the components of a mixture containing a solid and a liquid. (1.9)
- First law of thermodynamics** the energy of the universe is constant; same as the law of conservation of energy. (6.1)
- Fission** the process of using a neutron to split a heavy nucleus into two nuclei with smaller mass numbers. (18.6)
- Flotation process** a method of separating the mineral particles in an ore from the gangue that depends on the greater wettability of the mineral pieces. (21.8)
- Formal charge** the charge assigned to an atom in a molecule or polyatomic ion derived from a specific set of rules. (8.12)
- Formation constant (stability constant)** the equilibrium constant for each step of the formation of a complex ion by the addition of an individual ligand to a metal ion or complex ion in aqueous solution. (15.8)
- Fossil fuel** coal, petroleum, or natural gas; consists of carbon-based molecules derived from decomposition of once-living organisms. (6.5)
- Frasch process** the recovery of sulfur from underground deposits by melting it with hot water and forcing it to the surface by air pressure. (20.6)
- Free energy** a thermodynamic function equal to the enthalpy (H) minus the product of the entropy (S) and the Kelvin temperature (T); $G = H - TS$. Under certain conditions the change in free energy for a process is equal to the maximum useful work. (16.4)
- Free radical** a species with an unpaired electron. (22.5)
- Frequency** the number of waves (cycles) per second that pass a given point in space. (7.1)
- Fuel cell** a galvanic cell for which the reactants are continuously supplied. (17.5)
- Functional group** an atom or group of atoms in hydrocarbon derivatives that contains elements in addition to carbon and hydrogen. (22.4)
- Fusion** the process of combining two light nuclei to form a heavier, more stable nucleus. (18.6)
- Galvanic cell** a device in which chemical energy from a spontaneous redox reaction is changed to electrical energy that can be used to do work. (17.1)
- Galvanizing** a process in which steel is coated with zinc to prevent corrosion. (17.6)
- Gamma (γ) ray** a high-energy photon. (18.1)
- Gangue** the impurities (such as clay or sand) in an ore. (21.8)
- Geiger-Müller counter (Geiger counter)** an instrument that measures the rate of radioactive decay based on the ions and electrons produced as a radioactive particle passes through a gas-filled chamber. (18.4)
- Gene** a given segment of the DNA molecule that contains the code for a specific protein. (22.6)
- Geometrical (cis-trans) isomerism** isomerism in which atoms or groups of atoms can assume different positions around a rigid ring or bond. (21.4; 22.2)
- Glass** an amorphous solid obtained when silica is mixed with other compounds, heated above its melting point, and then cooled rapidly. (10.5)
- Glass electrode** an electrode for measuring pH from the potential difference that develops when it is dipped into an aqueous solution containing H^+ ions. (17.4)
- Glycosidic linkage** a $C-O-C$ bond formed between the rings of two cyclic monosaccharides by the elimination of water. (22.6)
- Graham's law of effusion** the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. (5.7)
- Greenhouse effect** a warming effect exerted by the earth's atmosphere (particularly CO_2 and H_2O) due to thermal energy retained by absorption of infrared radiation. (6.5)
- Ground state** the lowest possible energy state of an atom or molecule. (7.4)

Group (of the periodic table) a vertical column of elements having the same valence electron configuration and showing similar properties. (2.7)

Haber process the manufacture of ammonia from nitrogen and hydrogen, carried out at high pressure and high temperature with the aid of a catalyst. (3.9; 20.2)

Half-life (of a radioactive sample) the time required for the number of nuclides in a radioactive sample to reach half of the original value. (18.2)

Half-life (of a reactant) the time required for a reactant to reach half of its original concentration. (12.4)

Half-reactions the two parts of an oxidation–reduction reaction, one representing oxidation, the other reduction. (4.10; 17.1)

Halogen a Group 7A element. (2.7; 20.7)

Halogenation the addition of halogen atoms to unsaturated hydrocarbons. (22.2)

Hard water water from natural sources that contains relatively large concentrations of calcium and magnesium ions. (19.4)

Heat energy transferred between two objects due to a temperature difference between them. (6.1)

Heat capacity the amount of energy required to raise the temperature of an object by one degree Celsius. (6.2)

Heat of fusion the enthalpy change that occurs to melt a solid at its melting point. (10.8)

Heat of hydration the enthalpy change associated with placing gaseous molecules or ions in water; the sum of the energy needed to expand the solvent and the energy released from the solvent–solute interactions. (11.2)

Heat of solution the enthalpy change associated with dissolving a solute in a solvent; the sum of the energies needed to expand both solvent and solute in a solution and the energy released from the solvent–solute interactions. (11.2)

Heat of vaporization the energy required to vaporize one mole of a liquid at a pressure of one atmosphere. (10.8)

Heating curve a plot of temperature versus time for a substance where energy is added at a constant rate. (10.8)

Heisenberg uncertainty principle a principle stating that there is a fundamental limitation to how precisely both the position and momentum of a particle can be known at a given time. (7.5)

Heme an iron complex. (21.7)

Hemoglobin a biomolecule composed of four myoglobin-like units (proteins plus heme) that can bind and transport four oxygen molecules in the blood. (21.7)

Henderson–Hasselbalch equation an equation giving the relationship between the pH of an acid–base system and the concentrations of base and acid: $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$. (15.2)

Henry's law the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. (11.3)

Hess's law in going from a particular set of reactants to a particular set of products, the enthalpy change is the same whether the reaction takes place in one step or in a series of steps; in summary, enthalpy is a state function. (6.3)

Heterogeneous equilibrium an equilibrium involving reactants and/or products in more than one phase. (13.4)

Hexagonal closest packed (hcp) structure a structure composed of closest packed spheres with an *ababab* arrangement of layers; the unit cell is hexagonal. (10.4)

Homogeneous equilibrium an equilibrium system where all reactants and products are in the same phase. (13.4)

Homopolymer a polymer formed from the polymerization of only one type of monomer. (22.5)

Hund's rule the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a particular set of degenerate orbitals, with all unpaired electrons having parallel spins. (7.11)

Hybrid orbitals a set of atomic orbitals adopted by an atom in a molecule different from those of the atom in the free state. (9.1)

Hybridization a mixing of the native orbitals on a given atom to form special atomic orbitals for bonding. (9.1)

Hydration the interaction between solute particles and water molecules. (4.1)

Hydride a binary compound containing hydrogen. The hydride ion, H^- , exists in ionic hydrides. The three classes of hydrides are covalent, interstitial, and ionic. (19.3)

Hydrocarbon a compound composed of carbon and hydrogen. (22.1)

Hydrocarbon derivative an organic molecule that contains one or more elements in addition to carbon and hydrogen. (22.4)

Hydrogen bonding unusually strong dipole–dipole attractions that occur among molecules in which hydrogen is bonded to a highly electronegative atom. (10.1)

Hydrogenation reaction a reaction in which hydrogen is added, with a catalyst present, to a carbon–carbon multiple bond. (22.2)

Hydrohalic acid an aqueous solution of a hydrogen halide. (20.7)

Hydrometallurgy a process for extracting metals from ores by use of aqueous chemical solutions. Two steps are involved: selective leaching and selective precipitation. (21.8)

Hydronium ion the H_3O^+ ion; a hydrated proton. (14.1)

Hypothesis one or more assumptions put forth to explain the observed behavior of nature. (1.2)

Ideal gas law an equation of state for a gas, where the state of the gas is its condition at a given time; expressed by $PV = nRT$, where P = pressure, V = volume, n = moles of the gas, R = the universal gas constant, and T = absolute temperature. This equation expresses behavior approached by real gases at high T and low P . (5.3)

Ideal solution a solution whose vapor pressure is directly proportional to the mole fraction of solvent present. (11.4)

Indicator a chemical that changes color and is used to mark the end point of a titration. (4.8; 15.5)

Integrated rate law an expression that shows the concentration of a reactant as a function of time. (12.2)

Interhalogen compound a compound formed by the reaction of one halogen with another. (20.7)

Intermediate a species that is neither a reactant nor a product but that is formed and consumed in the reaction sequence. (12.6)

Intermolecular forces relatively weak interactions that occur between molecules. (10.1)

Internal energy a property of a system that can be changed by a flow of work, heat or both; $\Delta E = q + w$, where ΔE is the change in the internal energy of the system, q is heat, and w is work. (6.1)

Ion an atom or a group of atoms that has a net positive or negative charge. (2.6)

Ion exchange (water softening) the process in which an ion-exchange resin removes unwanted ions (for example, Ca^{2+} and Mg^{2+}) and replaces them with Na^+ ions, which do not interfere with soap and detergent action. (19.4)

Ion pairing a phenomenon occurring in solution when oppositely charged ions aggregate and behave as a single particle. (11.7)

Ion-product (dissociation) constant (K_w) the equilibrium constant for the auto-ionization of water; $K_w = [\text{H}^+][\text{OH}^-]$. At 25°C , K_w equals 1.0×10^{-14} . (14.2)

Ion-selective electrode an electrode sensitive to the concentration of a particular ion in solution. (17.4)

Ionic bonding the electrostatic attraction between oppositely charged ions. (2.6; 8.1)

Ionic compound (binary) a compound that results when a metal reacts with a nonmetal to form a cation and an anion. (8.1)

Ionic solid (salt) a solid containing cations and anions that dissolves in water to give a solution containing the separated ions which are mobile and thus free to conduct electrical current. (2.6; 10.3)

Irreversible process any real process. When a system undergoes the changes $\text{State 1} \rightarrow \text{State 2} \rightarrow \text{State 1}$ by any real pathway, the universe is different than before the cyclic process took place in the system. (16.9)

Isoelectronic ions ions containing the same number of electrons. (8.4)

Isomers species with the same formula but different properties. (21.4)

Isotactic chain a polymer chain in which the substituent groups such as CH_3 are all arranged on the same side of the chain. (22.5)

Isothnic solutions solutions having identical osmotic pressures. (11.6)

Isotopes atoms of the same element (the same number of protons) with different numbers of neutrons. They have identical atomic numbers but different mass numbers. (2.5; 18)

Ketone an organic compound containing the carbonyl group



bonded to two carbon atoms. (22.4)

Kinetic energy ($\frac{1}{2}mv^2$) energy due to the motion of an object; dependent on the mass of the object and the square of its velocity. (6.1)

Kinetic molecular theory (KMT) a model that assumes that an ideal gas is composed of tiny particles (molecules) in constant motion. (5.6)

Lanthanide contraction the decrease in the atomic radii of the lanthanide series elements, going from left to right in the periodic table. (21.1)

Lanthanide series a group of 14 elements following lanthanum in the periodic table, in which the $4f$ orbitals are being filled. (7.11; 19.1; 21.1)

Lattice a three-dimensional system of points designating the positions of the centers of the components of a solid (atoms, ions, or molecules). (10.3)

Lattice energy the energy change occurring when separated gaseous ions are packed together to form an ionic solid. (8.5)

Law of conservation of energy energy can be converted from one form to another but can be neither created nor destroyed. (6.1)

Law of conservation of mass mass is neither created nor destroyed. (1.2; 2.2)

Law of definite proportion a given compound always contains exactly the same proportion of elements by mass. (2.2)

Law of mass action a general description of the equilibrium condition; it defines the equilibrium constant expression. (13.2)

Law of multiple proportions a law stating that when two elements form a series of compounds, the ratios of the masses of the second element that combine with one gram of the first element can always be reduced to small whole numbers. (2.2)

Leaching the extraction of metals from ores using aqueous chemical solutions. (21.8)

Lead storage battery a battery (used in cars) in which the anode is lead, the cathode is lead coated with lead dioxide, and the electrolyte is a sulfuric acid solution. (17.5)

Le Châtelier's principle if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce the effect of that change. (13.7)

Lewis acid an electron-pair acceptor. (14.11)

Lewis base an electron-pair donor. (14.11)

Lewis structure a diagram of a molecule showing how the valence electrons are arranged among the atoms in the molecule. (8.10)

Ligand a neutral molecule or ion having a lone pair of electrons that can be used to form a bond to a metal ion; a Lewis base. (21.3)

Lime-soda process a water-softening method in which lime and soda ash are added to water to remove calcium and magnesium ions by precipitation. (14.6)

Limiting reactant (limiting reagent) the reactant that is completely consumed when a reaction is run to completion. (3.9)

Line spectrum a spectrum showing only certain discrete wavelengths. (7.3)

Linear accelerator a type of particle accelerator in which a changing electrical field is used to accelerate a positive ion along a linear path. (18.3)

Linkage isomerism isomerism involving a complex ion where the ligands are all the same but the point of attachment of at least one of the ligands differs. (21.4)

Liquefaction the transformation of a gas into a liquid. (19.1)

Localized electron (LE) model a model which assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. (8.9)

London dispersion forces the forces, existing among noble gas atoms and nonpolar molecules, that involve an accidental dipole that induces a momentary dipole in a neighbor. (10.1)

Lone pair an electron pair that is localized on a given atom; an electron pair not involved in bonding. (8.9)

Magnetic quantum number m_ℓ , the quantum number relating to the orientation of an orbital in space relative to the other orbitals with the same ℓ quantum number. It can have integral values between ℓ and $-\ell$, including zero. (7.6)

Main-group (representative) elements elements in the groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A in the periodic table. The group number gives the sum of the valence s and p electrons. (7.11; 18.1)

Major species the components present in relatively large amounts in a solution. (14.3)

Manometer a device for measuring the pressure of a gas in a container. (5.1)

Mass the quantity of matter in an object. (1.3)

Mass defect the change in mass occurring when a nucleus is formed from its component nucleons. (18.5)

Mass number the total number of protons and neutrons in the atomic nucleus of an atom. (2.5; 18)

Mass percent the percent by mass of a component of a mixture (11.1) or of a given element in a compound. (3.4)

Mass spectrometer an instrument used to determine the relative masses of atoms by the deflection of their ions on a magnetic field. (3.1)

Matter the material of the universe. (1.9)

Messenger RNA (mRNA) a special RNA molecule built in the cell nucleus that migrates into the cytoplasm and participates in protein synthesis. (22.6)

Metal an element that gives up electrons relatively easily and is lustrous, malleable, and a good conductor of heat and electricity. (2.7)

Metalloids (semimetals) elements along the division line in the periodic table between metals and nonmetals. These elements exhibit both metallic and nonmetallic properties. (7.13; 19.1)

Metallurgy the process of separating a metal from its ore and preparing it for use. (19.1; 21.8)

Millimeters of mercury (mmHg) a unit of pressure, also called a torr, $760 \text{ mm Hg} = 760 \text{ torr} = 101,325 \text{ Pa} = 1 \text{ standard atmosphere}$. (5.1)

Mineral a relatively pure compound as found in nature. (21.8)

Model (theory) a set of assumptions put forth to explain the observed behavior of matter. The models of chemistry usually involve assumptions about the behavior of individual atoms or molecules. (1.2)

Moderator a substance used in a nuclear reactor to slow down the neutrons. (18.6)

Molal boiling-point elevation constant a constant characteristic of a particular solvent that gives the change in boiling point as a function of solution molality; used in molecular weight determinations. (11.5)

Molal freezing-point depression constant a constant characteristic of a particular solvent that gives the change in freezing point as a function of the solution molality; used in molecular weight determinations (11.5)

Molality the number of moles of solute per kilogram of solvent in a solution. (11.1)

Molar heat capacity the energy required to raise the temperature of one mole of a substance by one degree Celsius. (6.2)

Molar mass the mass in grams of one mole of molecules or formula units of a substance; also called *molecular weight*. (3.3)

Molar volume the volume of one mole of an ideal gas; equal to 22.42 liters at STP. (5.4)

Molarity moles of solute per volume of solution in liters. (4.3; 11.1)

Mole (mol) the number equal to the number of carbon atoms in exactly 12 grams of pure ^{12}C ; Avogadro's number. One mole represents 6.022×10^{23} units. (3.2)

Mole fraction the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture. (5.5; 11.1)

Mole ratio (stoichiometry) the ratio of moles of one substance to moles of another substance in a balanced chemical equation. (3.8)

Molecular equation an equation representing a reaction in solution showing the reactants and products in undissociated form, whether they are strong or weak electrolytes. (4.6)

Molecular formula the exact formula of a molecule, giving the types of atoms and the number of each type. (3.5)

Molecular orbital (MO) model a model that regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule. In this model the electrons are assumed to be delocalized rather than always located between a given pair of atoms. (9.2; 10.4)

Molecular orientations (kinetics) orientations of molecules during collisions, some of which can lead to reaction while others cannot. (12.7)

Molecular solid a solid composed of neutral molecules at the lattice points. (10.3)

Molecular structure the three-dimensional arrangement of atoms in a molecule. (8.13)

Molecularity the number of species that must collide to produce the reaction represented by an elementary step in a reaction mechanism. (12.6)

Molecule a bonded collection of two or more atoms of the same or different elements. (2.6)

Monodentate (unidentate) ligand a ligand that can form one bond to a metal ion. (21.3)

Monoprotic acid an acid with one acidic proton. (14.2)

Monosaccharide (simple sugar) a polyhydroxy ketone or aldehyde containing from three to nine carbon atoms. (22.6)

Myoglobin an oxygen-storing biomolecule consisting of a heme complex and a proton. (21.7)

Natural law a statement that expresses generally observed behavior. (1.2)

Nernst equation an equation relating the potential of an electrochemical cell to the concentrations of the cell components:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q) \text{ at } 25^\circ\text{C} \quad (17.4)$$

Net ionic equation an equation for a reaction in solution, where strong electrolytes are written as ions, showing only those components that are directly involved in the chemical change. (4.6)

Network solid an atomic solid containing strong directional covalent bonds. (10.5)

Neutralization reaction an acid–base reaction. (4.8)

Neutron a particle in the atomic nucleus with mass virtually equal to the proton's but with no charge. (2.5; 18)

Nitrogen cycle the conversion of N_2 to nitrogen-containing compounds, followed by the return of nitrogen gas to the atmosphere by natural decay processes. (20.2)

Nitrogen fixation the process of transforming N_2 to nitrogen-containing compounds useful to plants. (20.2)

Nitrogen-fixing bacteria bacteria in the root nodules of plants that can convert atmospheric nitrogen to ammonia and other nitrogen-containing compounds useful to plants. (20.2)

Noble gas a Group 8A element. (2.7; 20.8)

Node an area of an orbital having zero electron probability. (7.7)

Nonelectrolyte a substance that, when dissolved in water, gives a nonconducting solution. (4.2)

Nonmetal an element not exhibiting metallic characteristics. Chemically, a typical nonmetal accepts electrons from a metal. (2.7)

Normal boiling point the temperature at which the vapor pressure of a liquid is exactly one atmosphere. (10.8)

Normal melting point the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure on the system is one atmosphere. (10.8)

Normality the number of equivalents of a substance dissolved in a liter of solution. (11.1)

Nuclear atom an atom having a dense center of positive charge (the nucleus) with electrons moving around the outside. (2.4)

Nuclear transformation the change of one element into another. (18.3)

Nucleon a particle in an atomic nucleus, either a neutron or a proton. (18)

Nucleotide a monomer of the nucleic acids composed of a five-carbon sugar, a nitrogen-containing base, and phosphoric acid. (22.6)

Nucleus the small, dense center of positive charge in an atom. (2.4)

Nuclide the general term applied to each unique atom; represented by ${}_Z^AX$, where X is the symbol for a particular element. (18)

Octet rule the observation that atoms of nonmetals tend to form the most stable molecules when they are surrounded by eight electrons (to fill their valence orbitals). (8.10)

Open hearth process a process for producing steel by oxidizing and removing the impurities in molten iron using external heat and a blast of air or oxygen. (21.8)

Optical isomerism isomerism in which the isomers have opposite effects on plane-polarized light. (21.4)

Orbital a specific wave function for an electron in an atom. The square of this function gives the probability distribution for the electron. (7.5)

d-Orbital splitting a splitting of the *d* orbitals of the metal ion in a complex such that the orbitals pointing at the ligands have higher energies than those pointing between the ligands. (21.6)

Order (of reactant) the positive or negative exponent, determined by experiment, of the reactant concentration in a rate law. (12.2)

Organic acid an acid with a carbon-atom backbone; often contains the carboxyl group. (14.2)

Organic chemistry the study of carbon-containing compounds (typically chains of carbon atoms) and their properties. (22)

Osmosis the flow of solvent into a solution through a semipermeable membrane. (11.6)

Osmotic pressure (π) the pressure that must be applied to a solution to stop osmosis; $\pi = MRT$. (11.6)

Ostwald process a commercial process for producing nitric acid by the oxidation of ammonia. (20.2)

Oxidation an increase in oxidation state (a loss of electrons). (4.9; 17.1)

Oxidation–reduction (redox) reaction a reaction in which one or more electrons are transferred. (4.9; 17.1)

Oxidation states a concept that provides a way to keep track of electrons in oxidation–reduction reactions according to certain rules. (4.9; 21.3)

Oxidizing agent (electron acceptor) a reactant that accepts electrons from another reactant. (4.9; 17.1)

Oxyacid an acid in which the acidic proton is attached to an oxygen atom. (14.2)

Ozone O_3 , the form of elemental oxygen in addition to the much more common O_2 . (20.5)

Paramagnetism a type of induced magnetism, associated with unpaired electrons, that causes a substance to be attracted into the inducing magnetic field. (9.3)

Partial pressures the independent pressures exerted by different gases in a mixture. (5.5)

Particle accelerator a device used to accelerate nuclear particles to very high speeds. (18.3)

Pascal the SI unit of pressure; equal to newtons per meter squared. (5.1)

Pauli exclusion principle in a given atom no two electrons can have the same set of four quantum numbers. (7.8)

Peptide linkage the bond resulting from the condensation reaction between amino acids; represented by:



Percent dissociation the ratio of the amount of a substance that is dissociated at equilibrium to the initial concentration of the substance in a solution, multiplied by 100. (14.5)

- Percent yield** the actual yield of a product as a percentage of the theoretical yield. (3.9)
- Periodic table** a chart showing all the elements arranged in columns with similar chemical properties. (2.7)
- pH curve (titration curve)** a plot showing the pH of a solution being analyzed as a function of the amount of titrant added. (15.4)
- pH scale** a log scale based on 10 and equal to $-\log[H^+]$; a convenient way to represent solution acidity. (14.3)
- Phase diagram** a convenient way of representing the phases of a substance in a closed system as a function of temperature and pressure. (10.9)
- Phenyl group** the benzene molecule minus one hydrogen atom. (22.3)
- Photochemical smog** air pollution produced by the action of light on oxygen, nitrogen oxides, and unburned fuel from auto exhaust to form ozone and other pollutants. (5.9)
- Photon** a quantum of electromagnetic radiation. (7.2)
- Physical change** a change in the form of a substance, but not in its chemical composition; chemical bonds are not broken in a physical change. (1.9)
- Pi (π) bond** a covalent bond in which parallel p orbitals share an electron pair occupying the space above and below the line joining the atoms. (9.1)
- Planck's constant** the constant relating the change in energy for a system to the frequency of the electromagnetic radiation absorbed or emitted; equal to 6.626×10^{-34} J s. (7.2)
- Polar covalent bond** a covalent bond in which the electrons are not shared equally because one atom attracts them more strongly than the other. (8.1)
- Polar molecule** a molecule that has a permanent dipole moment. (4.1)
- Polyatomic ion** an ion containing a number of atoms. (2.6)
- Polyelectronic atom** an atom with more than one electron. (7.9)
- Polymer** a large, usually chainlike molecule built from many small molecules (monomers). (22.5)
- Polymerization** a process in which many small molecules (monomers) are joined together to form a large molecule. (22.2)
- Polypeptide** a polymer formed from amino acids joined together by peptide linkages. (22.6)
- Polyprotic acid** an acid with more than one acidic proton. It dissociates in a stepwise manner, one proton at a time. (14.7)
- Porous disk** a disk in a tube connecting two different solutions in a galvanic cell that allows ion flow without extensive mixing of the solutions. (17.1)
- Porphyrin** a planar ligand with a central ring structure and various substituent groups at the edges of the ring. (21.7)
- Positional probability** a type of probability that depends on the number of arrangements in space that yield a particular state. (16.1)
- Positron production** a mode of nuclear decay in which a particle is formed having the same mass as an electron but opposite charge. The net effect is to change a proton to a neutron. (18.1)
- Potential energy** energy due to position or composition. (6.1)
- Precipitation reaction** a reaction in which an insoluble substance forms and separates from the solution. (4.5)
- Precision** the degree of agreement among several measurements of the same quantity; the reproducibility of a measurement. (1.4)
- Primary structure (of a protein)** the order (sequence) of amino acids in the protein chain. (22.6)
- Principal quantum number (n)** the quantum number relating to the size and energy of an orbital; it can have any positive integer value. (7.6)
- Probability distribution** the square of the wave function indicating the probability of finding an electron at a particular point in space. (7.5)
- Product** a substance resulting from a chemical reaction. It is shown to the right of the arrow in a chemical equation. (3.6)
- Protein** a natural high-molecular-weight polymer formed by condensation reactions between amino acids. (22.6)
- Proton** a positively charged particle in an atomic nucleus. (2.5; 18)
- Pure substance** a substance with constant composition. (1.9)
- Pyrometallurgy** recovery of a metal from its ore by treatment at high temperatures. (21.8)
- Quantization** the concept that energy can occur only in discrete units called *quanta*. (7.2)
- Rad** a unit of radiation dosage corresponding to 10^{-2} J of energy deposited per kilogram of tissue (from radiation absorbed dose). (18.7)
- Radioactive decay (radioactivity)** the spontaneous decomposition of a nucleus to form a different nucleus. (2.4; 18.1)
- Radiocarbon dating (carbon-14 dating)** a method for dating ancient wood or cloth based on the rate of radioactive decay of the nuclide $^{14}_6\text{C}$. (18.4)
- Radiotracer** a radioactive nuclide, introduced into an organism for diagnostic purposes, whose pathway can be traced by monitoring its radioactivity. (18.4)
- Random error** an error that has an equal probability of being high or low. (1.4)
- Raoult's law** the vapor pressure of a solution is directly proportional to the mole fraction of solvent present. (11.4)
- Rate constant** the proportionality constant in the relationship between reaction rate and reactant concentrations. (12.2)
- Rate of decay** the change in the number of radioactive nuclides in a sample per unit time. (18.2)
- Rate-determining step** the slowest step in a reaction mechanism, the one determining the overall rate. (12.6)
- Rate law (differential rate law)** an expression that shows how the rate of reaction depends on the concentration of reactants. (12.2)
- Reactant** a starting substance in a chemical reaction. It appears to the left of the arrow in a chemical equation. (3.6)
- Reaction mechanism** the series of elementary steps involved in a chemical reaction. (12.6)
- Reaction quotient Q** a quotient obtained by applying the law of mass action to initial concentrations rather than to equilibrium concentrations. (13.5)

- Reaction rate** the change in concentration of a reactant or product per unit time. (12.1)
- Reactor core** the part of a nuclear reactor where the fission reaction takes place. (18.6)
- Reducing agent (electron donor)** a reactant that donates electrons to another substance to reduce the oxidation state of one of its atoms. (4.9; 17.1)
- Reduction** a decrease in oxidation state (a gain of electrons). (4.9; 17.1)
- Rem** a unit of radiation dosage that accounts for both the energy of the dose and its effectiveness in causing biological damage (from roentgen equivalent for man). (18.7)
- Resonance** a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual electronic structure is not represented by any one of the Lewis structures but by the average of all of them. (8.12)
- Reverse osmosis** the process occurring when the external pressure on a solution causes a net flow of solvent through a semipermeable membrane from the solution to the solvent. (11.6)
- Reversible process** a cyclic process carried out by a hypothetical pathway, which leaves the universe exactly the same as it was before the process. No real process is reversible. (16.9)
- Ribonucleic acid (RNA)** a nucleotide polymer that transmits the genetic information stored in DNA to the ribosomes for protein synthesis. (22.6)
- Roasting** a process of converting sulfide minerals to oxides by heating in air at temperatures below their melting points. (21.8)
- Root mean square velocity** the square root of the average of the squares of the individual velocities of gas particles. (5.6)
- Salt** an ionic compound. (14.8)
- Salt bridge** a U-tube containing an electrolyte that connects the two compartments of a galvanic cell, allowing ion flow without extensive mixing of the different solutions. (17.1)
- Scientific method** the process of studying natural phenomena, involving observations, forming laws and theories, and testing of theories by experimentation. (1.1)
- Scintillation counter** an instrument that measures radioactive decay by sensing the flashes of light produced in a substance by the radiation. (18.4)
- Second law of thermodynamics** in any spontaneous process, there is always an increase in the entropy of the universe. (16.2)
- Secondary structure (of a protein)** the three-dimensional structure of the protein chain (for example, α -helix, random coil, or pleated sheet). (22.6)
- Selective precipitation** a method of separating metal ions from an aqueous mixture by using a reagent whose anion forms a precipitate with only one or a few of the ions in the mixture. (4.7; 15.7)
- Semiconductor** a substance conducting only a slight electrical current at room temperature, but showing increased conductivity at higher temperatures. (10.5)
- Semipermeable membrane** a membrane that allows solvent but not solute molecules to pass through. (11.6)
- SI system** International System of units based on the metric system and units derived from the metric system. (1.2)
- Side chain (of amino acid)** the hydrocarbon group on an amino acid represented by H, CH₃, or a more complex substituent. (22.6)
- Sigma (σ) bond** a covalent bond in which the electron pair is shared in an area centered on a line running between the atoms. (9.1)
- Significant figures** the certain digits and the first uncertain digit of a measurement. (1.4)
- Silica** the fundamental silicon-oxygen compound, which has the empirical formula SiO₂, and forms the basis of quartz and certain types of sand. (10.5)
- Silicates** salts that contain metal cations and polyatomic silicon-oxygen anions that are usually polymeric. (10.5)
- Single bond** a bond in which one pair of electrons is shared by two atoms. (8.8)
- Smelting** a metallurgical process that involves reducing metal ions to the free metal. (21.8)
- Solubility** the amount of a substance that dissolves in a given volume of solvent at a given temperature. (4.2)
- Solubility product constant** the constant for the equilibrium expression representing the dissolving of an ionic solid in water. (15.6)
- Solute** a substance dissolved in a liquid to form a solution. (4.2; 11.1)
- Solution** a homogeneous mixture. (1.9)
- Solvent** the dissolving medium in a solution. (4.2)
- Somatic damage** radioactive damage to an organism resulting in its sickness or death. (18.7)
- Space-filling model** a model of a molecule showing the relative sizes of the atoms and their relative orientations. (2.6)
- Specific heat capacity** the energy required to raise the temperature of one gram of a substance by one degree Celsius. (6.2)
- Spectator ions** ions present in solution that do not participate directly in a reaction. (4.6)
- Spectrochemical series** a listing of ligands in order based on their ability to produce *d*-orbital splitting. (21.6)
- Spontaneous fission** the spontaneous splitting of a heavy nuclide into two lighter nuclides. (18.1)
- Spontaneous process** a process that occurs without outside intervention. (16.1)
- Standard atmosphere** a unit of pressure equal to 760 mm Hg. (5.1)
- Standard enthalpy of formation** the enthalpy change that accompanies the formation of one mole of a compound at 25°C from its elements, with all substances in their standard states at that temperature. (6.4)
- Standard free energy change** the change in free energy that will occur for one unit of reaction if the reactants in their standard states are converted to products in their standard states. (16.6)
- Standard free energy of formation** the change in free energy that accompanies the formation of one mole of a substance from its constituent elements with all reactants and products in their standard states. (16.6)

- Standard hydrogen electrode** a platinum conductor in contact with 1 M H^+ ions and bathed by hydrogen gas at one atmosphere. (17.2)
- Standard reduction potential** the potential of a half-reaction under standard state conditions, as measured against the potential of the standard hydrogen electrode. (17.2)
- Standard solution** a solution whose concentration is accurately known. (4.3)
- Standard state** a reference state for a specific substance defined according to a set of conventional definitions. (6.4)
- Standard temperature and pressure (STP)** the condition 0°C and 1 atmosphere of pressure. (5.4)
- Standing wave** a stationary wave as on a string of a musical instrument; in the wave mechanical model, the electron in the hydrogen atom is considered to be a standing wave. (7.5)
- State function (property)** a property that is independent of the pathway. (6.1)
- States of matter** the three different forms in which matter can exist; solid, liquid, and gas. (1.9)
- Stereoisomerism** isomerism in which all the bonds in the isomers are the same but the spatial arrangements of the atoms are different. (21.4)
- Steric factor** the factor (always less than 1) that reflects the fraction of collisions with orientations that can produce a chemical reaction. (12.7)
- Stoichiometric quantities** quantities of reactants mixed in exactly the correct amounts so that all are used up at the same time. (3.9)
- Strong acid** an acid that completely dissociates to produce an H^+ ion and the conjugate base. (4.2; 14.2)
- Strong base** a metal hydroxide salt that completely dissociates into its ions in water. (4.2; 14.6)
- Strong electrolyte** a material that, when dissolved in water, gives a solution that conducts an electric current very efficiently. (4.2)
- Structural formula** the representation of a molecule in which the relative positions of the atoms are shown and the bonds are indicated by lines. (2.6)
- Structural isomerism** isomerism in which the isomers contain the same atoms but one or more bonds differ. (21.4; 22.1)
- Subcritical reaction (nuclear)** a reaction in which less than one neutron causes another fission event and the process dies out. (18.6)
- Sublimation** the process by which a substance goes directly from the solid to the gaseous state without passing through the liquid state. (10.8)
- Subshell** a set of orbitals with a given azimuthal quantum number. (7.6)
- Substitution reaction (hydrocarbons)** a reaction in which an atom, usually a halogen, replaces a hydrogen atom in a hydrocarbon. (22.1)
- Supercooling** the process of cooling a liquid below its freezing point without its changing to a solid. (10.8)
- Supercritical reaction (nuclear)** a reaction in which more than one neutron from each fission event causes another fission event. The process rapidly escalates to a violent explosion. (18.6)
- Superheating** the process of heating a liquid above its boiling point without its boiling. (10.8)
- Superoxide** a compound containing the O_2^- anion. (19.2)
- Surface tension** the resistance of a liquid to an increase in its surface area. (10.2)
- Surroundings** everything in the universe surrounding a thermodynamic system. (6.1)
- Syndiotactic chain** a polymer chain in which the substituent groups such as CH_3 are arranged on alternate sides of the chain. (22.5)
- Syngas** synthetic gas, a mixture of carbon monoxide and hydrogen, obtained by coal gasification. (6.6)
- System (thermodynamic)** that part of the universe on which attention is to be focused. (6.1)
- Systematic error** an error that always occurs in the same direction. (1.4)
- Tempering** a process in steel production that fine-tunes the proportions of carbon crystals and cementite by heating to intermediate temperatures followed by rapid cooling. (21.8)
- Termolecular step** a reaction involving the simultaneous collision of three molecules. (12.6)
- Tertiary structure (of a protein)** the overall shape of a protein, long and narrow or globular, maintained by different types of intramolecular interactions. (22.6)
- Theoretical yield** the maximum amount of a given product that can be formed when the limiting reactant is completely consumed. (3.9)
- Theory** a set of assumptions put forth to explain some aspect of the observed behavior of matter. (1.2)
- Thermal pollution** the oxygen-depleting effect on lakes and rivers of using water for industrial cooling and returning it to its natural source at a higher temperature. (11.3)
- Thermodynamic stability (nuclear)** the potential energy of a particular nucleus as compared to the sum of the potential energies of its component protons and neutrons. (18.1)
- Thermodynamics** the study of energy and its interconversions. (6.1)
- Thermoplastic polymer** a substance that when molded to a certain shape under appropriate conditions can later be remelted. (22.5)
- Thermoset polymer** a substance that when molded to a certain shape under pressure and high temperatures cannot be softened again or dissolved. (22.5)
- Third law of thermodynamics** the entropy of a perfect crystal at 0 K is zero. (16.5)
- Titration** a technique in which one solution is used to analyze another. (4.8)
- Torr** another name for millimeter of mercury (mm Hg). (5.1)
- Transfer RNA (tRNA)** a small RNA fragment that finds specific amino acids and attaches them to the protein chain as dictated by the codons in mRNA. (22.6)
- Transition metals** several series of elements in which inner orbitals (*d* or *f* orbitals) are being filled. (7.11; 19.1)

- Transuranium elements** the elements beyond uranium that are made artificially by particle bombardment. (18.3)
- Triple bond** a bond in which three pairs of electrons are shared by two atoms. (8.8)
- Triple point** the point on a phase diagram at which all three states of a substance are present. (10.9)
- Tyndall effect** the scattering of light by particles in a suspension. (11.8)
- Uncertainty (in measurement)** the characteristic that any measurement involves estimates and cannot be exactly reproduced. (1.4)
- Unimolecular step** a reaction step involving only one molecule. (12.6)
- Unit cell** the smallest repeating unit of a lattice. (10.3)
- Unit factor method** an equivalence statement between units used for converting from one unit to another. (1.6)
- Universal gas constant** the combined proportionality constant in the ideal gas law; $0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$ or $8.3145 \text{ J/K} \cdot \text{mol}$. (5.3)
- Valence electrons** the electrons in the outermost principal quantum level of an atom. (7.11)
- Valence shell electron-pair repulsion (VSEPR) model** a model whose main postulate is that the structure around a given atom in a molecule is determined principally by minimizing electron-pair repulsions. (8.13)
- Van der Waals equation** a mathematical expression for describing the behavior of real gases. (5.8)
- Van't Hoff factor** the ratio of moles of particles in solution to moles of solute dissolved. (11.7)
- Vapor pressure** the pressure of the vapor over a liquid at equilibrium. (10.8)
- Vaporization (evaporation)** the change in state that occurs when a liquid evaporates to form a gas. (10.8)
- Viscosity** the resistance of a liquid to flow. (10.2)
- Volt** the unit of electrical potential defined as one joule of work per coulomb of charge transferred. (17.1)
- Voltmeter** an instrument that measures cell potential by drawing electric current through a known resistance. (17.1)
- Volumetric analysis** a process involving titration of one solution with another. (4.8)
- Vulcanization** a process in which sulfur is added to rubber and the mixture is heated, causing crosslinking of the polymer chains and thus adding strength to the rubber. (22.5)
- Wave function** a function of the coordinates of an electron's position in three-dimensional space that describes the properties of the electron. (7.5)
- Wave mechanical model** a model for the hydrogen atom in which the electron is assumed to behave as a standing wave. (7.5)
- Wavelength** the distance between two consecutive peaks or troughs in a wave. (7.1)
- Weak acid** an acid that dissociates only slightly in aqueous solution. (4.2; 14.2)
- Weak base** a base that reacts with water to produce hydroxide ions to only a slight extent in aqueous solution. (4.2; 14.6)
- Weak electrolyte** a material which, when dissolved in water, gives a solution that conducts only a small electric current. (4.2)
- Weight** the force exerted on an object by gravity. (1.3)
- Work** force acting over a distance. (6.1)
- X-ray diffraction** a technique for establishing the structure of crystalline solids by directing X rays of a single wavelength at a crystal and obtaining a diffraction pattern from which interatomic spaces can be determined. (10.3)
- Zone of nuclear stability** the area encompassing the stable nuclides on a plot of their positions as a function of the number of protons and the number of neutrons in the nucleus. (18.1)
- Zone refining** a metallurgical process for obtaining a highly pure metal that depends on continuously melting the impure material and recrystallizing the pure metal. (21.8)



Answers to Selected Exercises

The answers listed here are from the *Complete Solutions Guide*, in which rounding is carried out at each intermediate step in a calculation in order to show the correct number of significant figures for that step. Therefore, an answer given here may differ in the last digit from the result obtained by carrying extra digits throughout the entire calculation and rounding at the end (the procedure you should follow).

Chapter 1

17. No, it is useful whenever a systematic approach of observation and hypothesis testing can be used. 19. Volume readings are estimated to one decimal place past the markings on the glassware. The assumed uncertainty is ± 1 in the estimated digit. **a.** The volume would be estimated to the tenths place since the markings are to ones place. A sample reading would be 4.2 with an uncertainty of ± 0.1 . This reading has two significant figures. **b.** 10.52 ± 0.01 would be a sample reading and the uncertainty; this reading has four significant figures. **c.** 18 ± 1 would be a sample reading and uncertainty, with the reading having two significant figures. 21. Chemical changes involve the making and breaking of chemical forces (bonds). Physical changes do not. The identity of a substance changes after a chemical change, but not after a physical change. 23. **a.** Inexact; **b.** Exact; **c.** Exact; $36 \text{ in/yd} \times 2.54 \text{ cm/in} \times 1 \text{ m/100 cm} = 0.9144 \text{ m/yd}$ (All conversion factors used are exact.) **d.** Inexact; the announced attendance is generally the number of tickets sold, not the number who were actually in the stadium. Some people who paid may not have gone, some may sneak in without paying, etc. **e.** Exact; **f.** Inexact 25. **a.** 2; **b.** 4; **c.** 4; **d.** 4; **e.** 3; **f.** 3; **g.** 4; **h.** 7 27. **a.** 3.13×10^2 ; **b.** 3.13×10^{-4} ; **c.** 3.13×10^7 ; **d.** 3.13×10^{-1} ; **e.** 3.13×10^{-2} 29. **a.** 102.623; **b.** 236.2; **c.** 3.0814; **d.** 4.67 31. **a.** 467; **b.** 0.24; **c.** 33.04; **d.** 75; **e.** 0.12; **f.** 0.21; **g.** 4.9; **h.** 0.01 33. **a.** 84.3 mm; **b.** 2.41 m; **c.** $2.945 \times 10^{-5} \text{ cm}$; **d.** 14.45 km; **e.** $2.353 \times 10^5 \text{ mm}$; **f.** $0.9033 \mu\text{m}$ 35. **a.** 8 lb and 9.9 oz; $20\frac{1}{2} \text{ in}$; **b.** $4.0 \times 10^4 \text{ km}$, $4.0 \times 10^7 \text{ m}$; **c.** $1.2 \times 10^{-2} \text{ m}^3$, 12 L , 730 in^3 , 0.42 ft^3 37. **a.** $4.00 \times 10^2 \text{ rods}$; 10.0 furlongs ; $2.01 \times 10^3 \text{ m}$; 2.01 km ; **b.** 8390.0 rods ; 209.75 furlongs ; $42,195 \text{ m}$; 42.195 km 39. **a.** 0.373 kg, 0.822 lb; **b.** 31.1 g, 156 carats; **c.** 19.3 cm^3 41. $2.95 \times 10^9 \text{ knots}$ 43. The spouse's car, with 33 mi/gal, has the better gas mileage. 45. \$1.59 47. 39.2°C , 312.4 K 49. **a.** 351.3 K ; 173°F ; **b.** 248 K ; -13°F ; **c.** 0 K ; -459°F ; **d.** 1074 K ; 1470°F 51. $69.1 \pm 0.2^\circ\text{F}$ 53. $2.70 \times 10^3 \text{ kg/m}^3$, 169 lb/ft^3 55. $1 \times 10^6 \text{ g/cm}^3$ 57. 0.28 cm^3 59. 3.8 g/cm^3 61. **a.** Both are the same mass; **b.** 1.0 mL mercury; **c.** Both are the same mass; **d.** 1.0 L benzene 63. 2.77 cm 65. Solid: own volume, own shape, does not flow. Liquid: own volume, takes shape of container, flows. Gas: takes volume and shape of container, flows 67. **a.** Picture iv represents a gaseous compound. Pictures ii and iii also contain a gaseous compound but have a gaseous element present. **b.** Picture vi represents a mixture of two elemental gases. **c.** Picture v represents a solid element. **d.** Pictures ii and iii both represent a mixture of a gaseous element and a gaseous compound. 69. **a.** physical; **b.** chemical; **c.** physical; **d.** chemical 71. $6.02 \times 10^{17} \text{ atoms}$; $2.08 \times 10^{-4} \text{ mol}$ 73. $1.0 \times 10^5 \text{ bags}$ 75. $7 \times 10^5 \text{ kg}$ 77. **a.** Volume $\times$ density = mass; the orange block is more dense. Since mass (orange) $>$ mass (blue) and volume (orange) $<$ volume (blue), then the density of the orange block must be greater to account for the larger mass of the orange block. **b.** Which block is more dense cannot be determined. Since mass (orange) $>$ mass (blue) and volume (orange) $>$ volume (blue), then the density of the orange block may or may not be larger than the blue block. If the blue block is more dense,

then its density cannot be so large that the mass of the smaller blue block becomes larger than the orange block mass. **c.** The blue block is more dense. Since mass (blue) = mass (orange) and volume (blue) $<$ volume (orange), then the density of the blue block must be larger to equate the masses. **d.** The blue block is more dense. Since mass (blue) $>$ mass (orange) and the volumes are equal, then the density of the blue block must be larger to give the blue block the larger mass. 79. $8.5 \pm 0.5 \text{ g/cm}^3$ 81. In a subtraction, the result gets smaller, but the uncertainties are added. If the two numbers are very close, the uncertainty may be larger than the result. 83. $d_{\text{old}} = 8.8 \text{ g/cm}^3$, $d_{\text{new}} = 7.17 \text{ g/cm}^3$; $d_{\text{new}}/d_{\text{old}} = \text{mass}_{\text{new}}/\text{mass}_{\text{old}} = 0.81$; The difference in mass is accounted for by the difference in the alloy used (if the assumptions are correct). 85. **a.** One possibility is that rope B is not attached to anything and rope A and rope C are connected via a pair of pulleys and/or gears; **b.** Try to pull rope B out of the box. Measure the distance moved by C for a given movement of A. Hold either A or C firmly while pulling on the other rope.

Chapter 2

15. **a.** Atoms have mass and are neither destroyed nor created by chemical reactions. Therefore, mass is neither created nor destroyed by chemical reactions. Mass is conserved. **b.** The composition of a substance depends on the number and kinds of atoms that form it. **c.** Compounds of the same elements differ only in the numbers of atoms of the elements forming them, i.e., NO, N_2O , NO_2 . 17. Deflection of cathode rays by magnetic and electric fields led to the conclusion that they were negatively charged. The cathode ray was produced at the negative electrode and repelled by the negative pole of the applied electric field. 19. The proton and the neutron have similar mass, with the mass of the neutron being slightly larger than that of the proton. Each of these particles has a mass approximately 1800 times greater than that of an electron. The combination of the protons and the neutrons in the nucleus make up the bulk of the mass of an atom, but the electrons make the greatest contribution to the chemical properties of the atom. 21. The atomic number of an element is equal to the number of protons in the nucleus of an atom of that element. The mass number is the sum of the number of protons and neutrons in the nucleus. The atomic mass is the actual mass of a particular isotope (including electrons). As we will see in Chapter 3, the average mass of an atom is taken from a measurement made on a large number of atoms. The average atomic mass value is listed in the periodic table. 23. A compound will always contain the same numbers (and types) of atoms. A given amount of hydrogen will react only with a specific amount of oxygen. Any excess oxygen will remain unreacted. 25. **a.** The composition of a substance depends on the number of atoms of each element making up the compound (depends on the formula of the compound) and not on the composition of the mixture from which it was formed. **b.** Avogadro's hypothesis implies that volume ratios are equal to molecule ratios at constant temperature and pressure. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{ HCl}(\text{g})$; from the balanced equation, the volume of HCl produced will be twice the volume of H_2 (or Cl_2) reacted. 27. The F-to-S mass ratios are simple whole numbers, 1:2:3. 29. O, 7.94; Na, 22.8; Mg, 11.9; O and Mg are incorrect by a factor of ≈ 2 ; correct formulas are H_2O , Na_2O , and MgO . 31. Using $r = 5 \times 10^{-14} \text{ cm}$, $d_{\text{nucleus}} = 3 \times 10^{15} \text{ g/cm}^3$; using $r = 1 \times 10^{-8} \text{ cm}$, $d_{\text{atom}} = 0.4 \text{ g/cm}^3$ 33. 37 35. sodium, Na; beryllium, Be; manganese, Mn; chromium, Cr; uranium, U 37. Sn: tin, Pt: platinum, Co: cobalt, Ni: nickel, Mg: magnesium, Ba: barium, K: potassium. 39. The noble gases are He, Ne, Ar,

Kr, Xe, and Rn (helium, neon, argon, krypton, xenon, and radon). All isotopes of radon are radioactive. **41.** a. 8; b. 8; c. 18; d. 5 **43.** a. 94 p, 144 n; b. 29 p, 36 n; c. 24 p, 28 n; d. 2 p, 2 n; e. 27 p, 33 n; f. 24 p, 30 n **45.** a. $^{12}_5\text{B}$; b. $^{15}_7\text{N}$; c. $^{35}_{17}\text{Cl}$; d. $^{235}_{92}\text{U}$; e. $^{14}_6\text{C}$; f. $^{31}_{15}\text{P}$ **47.** $^{153}_{63}\text{Eu}^{3+}$; $^{118}_{50}\text{Sn}^{2+}$ **49.** $^{75}_{33}\text{As}^{3+}$, 30 e; $^{128}_{52}\text{Te}^{2-}$, 52 p, 76 n, 2-; $^{32}_{16}\text{S}$, 0; $^{204}_{81}\text{Ti}^{+}$, 80 e; $^{195}_{78}\text{Pt}$, 78 p, 117 n, 78 e, 0 **51.** Metals: Mg, Ti, Au, Bi, Ge, Eu, Am; Non-metals: Si, B, At, Rn, Br **53.** a, d **55.** Metallic character increases down a group. **57.** a. lose, Na^{+} ; b. lose, Sr^{2+} ; c. lose, Ba^{2+} ; d. gain, I^{-} ; e. lose, Al^{3+} ; f. gain, S^{2-} **59.** a. sodium chloride; b. rubidium oxide; c. calcium sulfide; d. aluminum iodide **61.** a. chromium(VI) oxide; b. chromium(III) oxide; c. aluminum oxide; d. sodium hydride; e. calcium bromide; f. zinc chloride **63.** a. potassium perchlorate; b. calcium phosphate; c. aluminum sulfate; d. lead(II) nitrate **65.** a. nitrogen triiodide; b. sulfur difluoride; c. phosphorus trichloride; d. dinitrogen tetrafluoride **67.** a. copper(I) iodide; b. copper(II) iodide; c. cobalt(II) iodide; d. sodium carbonate; e. sodium hydrogen carbonate or sodium bicarbonate; f. tetrasulfur tetranitride; g. sulfur hexafluoride; h. sodium hypochlorite; i. barium chromate; j. ammonium nitrate **69.** a. CsBr ; b. BaSO_4 ; c. NH_4Cl ; d. ClO ; e. SiCl_4 ; f. ClF_3 ; g. BeO ; h. MgF_2 **71.** a. Na_2O ; b. Na_2O_2 ; c. KCN ; d. $\text{Cu}(\text{NO}_3)_2$; e. SeBr_4 ; f. PbS ; g. PbS_2 ; h. CuCl ; i. GaAs (from the positions in the periodic table, Ga^{3+} and As^{3-} are the predicted ions); j. CdSe ; k. ZnS ; l. HNO_2 ; m. P_2O_5 **73.** Yes, 1.0 g H would react with 37.0 g ^{37}Cl and 1.0 g H would react with 35.0 g ^{35}Cl . No, the mass ratio of H/Cl would always be 1 g H/37 g Cl for ^{37}Cl and 1 g H/35 g Cl for ^{35}Cl . As long as we had pure ^{35}Cl or pure ^{37}Cl , these ratios will always hold. If we have a mixture (such as the natural abundance of chlorine), the ratio will also be constant as long as the composition of the mixture of the two isotopes does not change. **75.** a. nitric acid; b. perchloric acid; c. acetic acid; d. sulfuric acid; e. phosphoric acid **77.** a. lead(II) acetate; b. copper(II) sulfate; c. calcium oxide; d. magnesium sulfate; e. magnesium hydroxide; f. calcium sulfate; g. dinitrogen monoxide or nitrous oxide (common) **79.** All contain 12 hydrogen atoms. **81.** a. Ca_3N_2 ; calcium nitride; b. K_2O ; potassium oxide; c. RbF ; rubidium fluoride; d. MgS ; magnesium sulfide; e. BaI_2 ; barium iodide; f. Al_2Se_3 ; aluminum selenide; g. Cs_3P ; cesium phosphide; h. InBr_3 ; indium(III) bromide (In forms compounds with +1 and +3 ions. You would predict a +3 ion from the position of In in the periodic table.) **83.** Cu, Ag, and Au **85.** The ratio of the masses of R that combine with 1.00 g Q is 3:1, as expected by the law of multiple proportions. R_3Q is the formula of the first compound. **87.** a. The compounds are isomers of each other. Isomers are compounds with the same formula but the atoms are attached differently, resulting in different properties. b. When wood burns, most of the solid material is converted to gases, which escape. c. Atoms are not an indivisible particle. Atoms are composed of electrons, neutrons, and protons. d. The two hydride samples contain different isotopes of either hydrogen and/or lithium. Isotopes may have different masses but have similar chemical properties.

Chapter 3

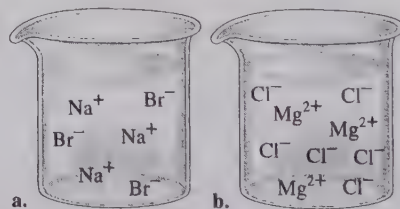
19. The molecular formula gives the actual number of atoms of each element in a molecule (or formula unit) of a compound. The empirical formula gives the simplest whole-number ratio of atoms of each element in a molecule. The molecular formula is a whole number multiple of the empirical formula. If that multiplier is one, the molecular and empirical formulas are the same. **21.** 24.31 amu **23.** 48% ^{151}Eu and 52% ^{153}Eu **25.** There are three peaks in the mass spectrum, each 2 mass units apart. This is consistent with two isotopes, differing in mass by two mass units. **27.** 4.64×10^{-20} g Fe **29.** 1.00×10^{22} atoms C **31.** Al_2O_3 , 101.96 g/mol; Na_3AlF_6 , 209.95 g/mol **33.** a. 17.03 g/mol; b. 32.05 g/mol; c. 252.08 g/mol **35.** a. 0.0587 mol NH_3 ; b. 0.0312 mol N_2H_4 ; c. 3.97×10^{-3} mol $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **37.** a. 85.2 g NH_3 ; b. 160. g N_2H_4 ; c. 1260 g $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **39.** a. 70.1 g N; b. 140. g N; c. 140. g N **41.** a. 3.54×10^{22} molecules NH_3 ; b. 1.88×10^{22} molecules N_2H_4 ;

c. 2.39×10^{21} formula units $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **43.** a. 3.54×10^{22} atoms N; b. 3.76×10^{22} atoms N; c. 4.78×10^{21} atoms N **45.** 176.12 g/mol; 2.839×10^{-3} mol; 1.710×10^{21} molecules **47.** a. 4.13×10^{-4} mol; b. 9.40×10^{-2} mol; c. 1.661×10^{-22} mol; d. 6.592×10^{-5} mol **49.** a. 5.59×10^{-2} g; b. 4.00 g; c. 0.433 g; d. 4.653×10^{-23} g; e. 1.00×10^4 g **51.** a. 294.30 g/mol; b. 3.40×10^{-2} mol; c. 459 g; d. 1.0×10^{19} molecules; e. 4.9×10^{21} atoms; f. 4.9×10^{-13} g; g. 4.887×10^{-22} g **53.** 13.35% Y, 41.22% Ba, 28.62% Cu, 16.81% O **55.** $\text{NO}_2 = \text{N}_2\text{O}_4 < \text{NO} < \text{N}_2\text{O}$ **57.** 1360 g/mol **59.** a. 39.99% C, 6.713% H, 53.30% O; b. 40.00% C, 6.714% H, 53.29% O; c. 40.00% C, 6.714% H, 53.29% O (all the same except for rounding differences) **61.** a. NO_2 ; b. CH_2 ; c. P_2O_5 ; d. CH_2O **63.** TiO_2 **65.** compound I: HgO ; compound II: Hg_2O **67.** NO_2 , N_2O_4 **69.** $\text{C}_3\text{H}_5\text{O}_2$; $\text{C}_6\text{H}_{10}\text{O}_4$ **71.** C_3H_8 **73.** C_3H_4 , C_6H_{12} **75.** a. $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$; b. $\text{Ca}(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(aq) + \text{H}_2(g)$; c. $\text{Ba}(\text{OH})_2(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{H}_2\text{O}(l)$ **77.** a. $\text{Cu}(s) + 2\text{AgNO}_3(aq) \rightarrow 2\text{Ag}(s) + \text{Cu}(\text{NO}_3)_2(aq)$; b. $\text{Zn}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$; c. $\text{Au}_2\text{S}_3(s) + 3\text{H}_2(g) \rightarrow 2\text{Au}(s) + 3\text{H}_2\text{S}(g)$ **79.** a. $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$; b. $\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g)$; c. $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 11\text{H}_2\text{O}(g)$; d. $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$; e. $4\text{FeO}(s) + \text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$ **81.** a. $\text{SiO}_2(s) + 2\text{C}(s) \rightarrow \text{Si}(s) + 2\text{CO}(g)$; b. $\text{SiCl}_4(l) + 2\text{Mg}(s) \rightarrow \text{Si}(s) + 2\text{MgCl}_2(s)$; c. $\text{Na}_2\text{SiF}_6(s) + 4\text{Na}(s) \rightarrow \text{Si}(s) + 6\text{NaF}(s)$ **83.** $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq) + \text{H}_2\text{O}(l) \rightarrow 4\text{C}_2\text{H}_5\text{OH}(aq) + 4\text{CO}_2(g)$ **85.** 6.51 g Cr_2O_3 , 1.20 g N_2 , 3.09 g H_2O **87.** 4.355 kg **89.** 7.2×10^4 g coke **91.** a. 65.01% Pt; 9.337% N; 2.015% H; 23.63% Cl; b. 72.3 g $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$; 35.9 g KCl **93.** a. stoichiometric mixture; b. I_2 ; c. Mg; d. Mg; e. stoichiometric mixture; f. I_2 ; g. stoichiometric mixture; h. I_2 ; i. Mg **95.** a. 18.0 g HgBr_2 ; 1.03 g Br_2 excess; b. 35.0 g HgBr_2 **97.** 1300 g CaSO_4 , 630 g H_3PO_4 **99.** 82.8% **101.** 1.20×10^3 kg = 1.20 metric tons **103.** Mn, 54.94 amu **105.** 9.25×10^{22} H atoms **107.** 4.30×10^{-2} mol; 2.50 g **109.** 5 **111.** 42.8% **113.** 86.2% **115.** $\text{C}_{20}\text{H}_{30}\text{O}$ **117.** $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ **119.** 1.8×10^6 g $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$; 5.9×10^5 g NH_3 **121.** 207 amu, Pb **123.** Al_2Se_3 **125.** 0.48 mol

Chapter 4

9. Solubility refers to how much dissolves. Electrolyte refers to whether or not ions are produced.

11.



c. For answers c–i, we will describe what should be in each solution. For c, the drawing should have three times as many NO_3^- anions as Al^{3+} cations. d. The drawing should have twice as many NH_4^+ cations as SO_4^{2-} anions. e. The drawing should have equal numbers of Na^+ cations and OH^- anions. f. The drawing should have equal numbers of Fe^{2+} cations and SO_4^{2-} anions. g. The drawing should have equal numbers of K^+ cations and MnO_4^- anions. h. The drawing should have equal numbers of H^+ cations and ClO_4^- anions. i. The drawing should have equal numbers of NH_4^+ cations and $\text{C}_2\text{H}_3\text{O}_2^-$ anions. **13.** $\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)$ **15.** a. 0.2677 M; b. 1.255×10^{-3} M; c. 8.065×10^{-3} M **17.** a. $M_{\text{Ca}^{2+}} = 0.15$ M, $M_{\text{Cl}^-} = 0.30$ M; b. $M_{\text{Al}^{3+}} = 0.26$ M, $M_{\text{NO}_3^-} = 0.78$ M; c. $M_{\text{K}^+} = 0.50$ M, $M_{\text{Cr}_2\text{O}_7^{2-}} = 0.25$ M; d. $M_{\text{Al}^{3+}} = 4.0 \times 10^{-3}$ M, $M_{\text{SO}_4^{2-}} = 6.0 \times 10^{-3}$ M **19.** 100.0 mL of 0.30 M AlCl_3 **21.** 41.7 mL **23.** a. Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH and fill to the mark. b. Add 500. mL of the 1.00 M NaOH stock solution to a 2-L volumetric flask; fill to the mark with water. c. As in a, instead using 38.8 g K_2CrO_4 . d. As in b, instead using 114 mL of 1.75 M K_2CrO_4 stock

solution. **25.** $M_{\text{NH}_4^+} = 0.272 \text{ M}$, $M_{\text{SO}_4^{2-}} = 0.136 \text{ M}$ **27.** $5.94 \times 10^{-8} \text{ M}$ steroid **29.** $\text{BaSO}_4(\text{s})$; **b.** $\text{PbCl}_2(\text{s})$; **c.** $\text{Ag}_3\text{PO}_4(\text{s})$; **d.** $\text{Fe}(\text{OH})_3(\text{s})$ **31. a.** $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; **b.** $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{K}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + 2\text{K}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; **c.** $3\text{AgNO}_3(\text{aq}) + \text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{NaNO}_3(\text{aq})$; $3\text{Ag}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq}) + 3\text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{Na}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq})$; $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$; **d.** $3\text{NaOH}(\text{aq}) + \text{Fe}(\text{NO}_3)_3(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaNO}_3(\text{aq})$; $3\text{Na}^+(\text{aq}) + 3\text{OH}^-(\text{aq}) + \text{Fe}^{3+}(\text{aq}) + 3\text{NO}_3^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{Na}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq})$; $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$ **33. a.** $\text{CuSO}_4(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \rightarrow \text{CuS}(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$; $\text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{CuS}(\text{s})$; the grey spheres are the Na^+ spectator ions and the blue-green spheres are the SO_4^{2-} spectator ions; **b.** $\text{CoCl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s}) + 2\text{NaCl}(\text{aq})$; $\text{Co}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s})$; the grey spheres are the Na^+ spectator ions and the green spheres are the Cl^- spectator ions; **c.** $\text{AgNO}_3(\text{aq}) + \text{KI}(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{KNO}_3(\text{aq})$; $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$; the red spheres are the K^+ spectator ions and the blue spheres are the NO_3^- spectator ions **35. a.** $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; **b.** $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; **c.** No reaction; **d.** No reaction; **e.** $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{s})$ **37.** Three possibilities are: addition of K_2SO_4 solution to give a white ppt. of PbSO_4 ; addition of NaCl to give a white ppt. of PbCl_2 ; addition of K_2CrO_4 solution to give a bright yellow ppt. of PbCrO_4 **39.** 0.607 g **41.** 0.520 g $\text{Al}(\text{OH})_3$ **43.** 2.9 g AgCl ; 0 M Ag^+ ; 0.10 M NO_3^- ; 0.075 M Ca^{2+} ; 0.050 M Cl^- **45. a.** $2\text{HClO}_4(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}(\text{ClO}_4)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $2\text{H}^+(\text{aq}) + 2\text{ClO}_4^-(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{ClO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $2\text{H}^+(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; **b.** $\text{HCN}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCN}(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{HCN}(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{HCN}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CN}^-(\text{aq})$; **c.** $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ **47. a.** $\text{KOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{KNO}_3(\text{aq})$; $\text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$; $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$; **b.** $\text{Ba}(\text{OH})_2(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{BaCl}_2(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$; **c.** $3\text{HClO}_4(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}(\text{ClO}_4)_3(\text{aq})$; $3\text{H}^+(\text{aq}) + 3\text{ClO}_4^-(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}^{3+}(\text{aq}) + 3\text{ClO}_4^-(\text{aq})$; $3\text{H}^+(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}^{3+}(\text{aq})$ **49. a.** 100. mL; **b.** 66.7 mL; **c.** 50.0 mL **51.** Basic, 0.250 M NO_3^- , 2.50 M Na^+ , 2.25 M OH^- **53.** 0.102 M **55.** 0.4178 g **57. a.** K, +1; O, -2; Mn, +7; **b.** Ni, +4; O, -2; **c.** Fe, +2; **d.** H, +1; O, -2; N, -3; P, +5; **e.** P, +3; O, -2; **f.** O, -2; Fe, +3; **g.** O, -2; F, -1; Xe, -6; **h.** S, +4; F, -1; **i.** C, +2; O, -2; **j.** Na, +1; O, -2; C, +3 **59. a.** Br, -1; **b.** Br, +1; **c.** Br, 0; **d.** Br, +7; **e.** Br, +3

61. Redox?	Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. Yes	O_2	CH_4	$\text{CH}_4(\text{C})$	$\text{O}_2(\text{O})$
b. Yes	HCl	Zn	Zn	$\text{HCl}(\text{H})$
c. No	—	—	—	—
d. Yes	O_3	NO	$\text{NO}(\text{N})$	$\text{O}_3(\text{O})$
e. Yes	H_2O_2	H_2O_2	$\text{H}_2\text{O}_2(\text{O})$	$\text{H}_2\text{O}_2(\text{O})$
f. Yes	CuCl	CuCl	$\text{CuCl}(\text{Cu})$	$\text{CuCl}(\text{Cu})$

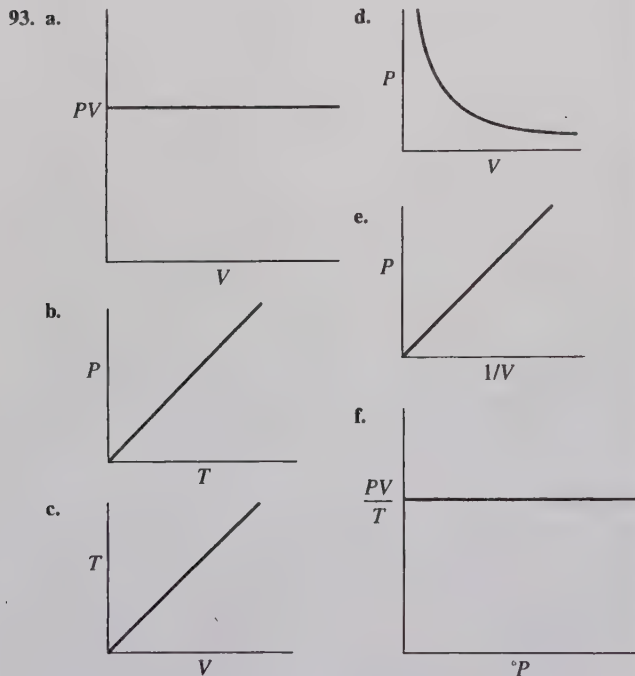
63. a. $\text{Zn} + 2\text{HCl} \rightarrow \text{Zn}^{2+} + \text{H}_2 + 2\text{Cl}^-$; **b.** $2\text{H}^+ + 3\text{I}^- + \text{ClO}^- \rightarrow \text{I}_3^- + \text{Cl}^- + \text{H}_2\text{O}$; **c.** $7\text{H}_2\text{O} + 4\text{H}^+ + 3\text{As}_2\text{O}_3 + 4\text{NO}_3^- \rightarrow 4\text{NO} + 6\text{H}_3\text{AsO}_4$; **d.** $16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Br}^- \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$; **e.** $8\text{H}^+ + 3\text{CH}_3\text{OH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 3\text{CH}_2\text{O} + 7\text{H}_2\text{O}$ **65. a.** $2\text{H}_2\text{O} + \text{Al} + \text{MnO}_4^- \rightarrow \text{Al}(\text{OH})_4^- + \text{MnO}_2$; **b.** $2\text{OH}^- + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$; **c.** $\text{OH}^- + \text{H}_2\text{O} + \text{NO}_2^- + 2\text{Al} \rightarrow \text{NH}_3 + 2\text{AlO}_2^-$ **67.** $4\text{NaCl} +$

$2\text{H}_2\text{SO}_4 + \text{MnO}_2 \rightarrow 2\text{Na}_2\text{SO}_4 + \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ **69.** 0.0111 M **71. a.** AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, and $\text{Hg}_2(\text{NO}_3)_2$ would form precipitates with the Cl^- ion; $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s})$; **b.** Na_2SO_4 , Na_2CO_3 , and Na_3PO_4 would form precipitates with the Ca^{2+} ion; $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$; $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$; $3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$; **c.** NaOH , Na_2S , and Na_2CO_3 would form precipitates with the Fe^{3+} ion; $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$; $2\text{Fe}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq}) \rightarrow \text{Fe}_2\text{S}_3(\text{s})$; $2\text{Fe}^{3+}(\text{aq}) + 3\text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Fe}_2(\text{CO}_3)_3(\text{s})$; **d.** BaCl_2 , $\text{Pb}(\text{NO}_3)_2$, and $\text{Ca}(\text{NO}_3)_2$ would form precipitates with the SO_4^{2-} ion; $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; $\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$; $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$; **e.** Na_2SO_4 , NaCl , and NaI would form precipitates with the Hg_2^{2+} ion; $\text{Hg}_2^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Hg}_2\text{SO}_4(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Hg}_2\text{I}_2(\text{s})$; **f.** NaBr , Na_2CrO_4 , and Na_3PO_4 would form precipitates with the Ag^+ ion; $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$; $2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s})$; $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$ **73.** 18.8 g **75.** 39.49 mg/tablet; 67.00% **77.** 2.00 M **79. a.** 0.8393 M; **b.** 5.010% **81.** $\text{C}_6\text{H}_6\text{O}$ **83.** $2\text{H}^+(\text{aq}) + \text{Mn}^{2+} + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$; $3\text{H}_2\text{O}(\text{l}) + 2\text{Mn}^{2+}(\text{aq}) + 5\text{IO}_4^-(\text{aq}) \rightarrow 2\text{MnO}_4^-(\text{aq}) + 5\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq})$ **85. a.** 24.8% Co, 29.7% Cl, 5.09% H, 40.4% O; **b.** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; **c.** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow 2\text{AgCl}(\text{s}) + \text{Co}(\text{NO}_3)_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s}) + 2\text{NaCl}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$; $4\text{Co}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Co}_2\text{O}_3(\text{s}) + 4\text{H}_2\text{O}(\text{l})$ **87. a.** 7.000 M K^+ ; **b.** 0.750 M CrO_4^{2-} **89.** 0.123 g SO_4^{2-} , 60.0% SO_4^{2-} ; 61% K_2SO_4 and 39% Na_2SO_4 **91.** 57.6 mL **93. a.** $\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{Mg}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $\text{Al}(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; **b.** MgO **95.** Citric acid has three acidic hydrogens per citric acid molecule. **97.** $0.07849 \pm 0.00016 \text{ M}$ or $0.0785 \pm 0.0002 \text{ M}$

Chapter 5

17. At constant n and T , $nRT = \text{constant}$, so $PV = k$ (Boyle's law). At constant P and n , $V = nRT/P = kT$ (Charles's law). **19.** The kinetic molecular theory assumes that gases do not exert forces on each other and that gas molecules are volumeless. Real gases do exert attractive forces on each other and real gases do have a volume. A gas behaves most ideally at low pressures and high temperatures. The effect of attractive forces is minimized at high temperatures since the gas molecules are moving very rapidly. At low pressure, the container volume is relatively large (P and V are inversely related) so the volume of the container that is taken up by the gas molecules is negligible. **21.** Graham's law of effusion can be used. Determine the relative effusion rate of the unknown gas to some known gas; then use Graham's law to determine the molar mass of the unknown. The ideal gas law also can be used to determine the molar mass. The appropriate form to use is molar mass $= dRT/P$. If the density, temperature, and pressure of the gas are known, then the molar mass can be calculated. **23.** Rigid container: pressure decreases (is halved) and the density is constant; flexible container: pressure is constant and the density increases (is doubled) **25. a.** $3.6 \times 10^3 \text{ mm Hg}$; **b.** $3.6 \times 10^3 \text{ torr}$; **c.** $4.9 \times 10^5 \text{ Pa}$; **d.** 71 psi **27.** 65 torr, $8.7 \times 10^3 \text{ Pa}$, $8.6 \times 10^{-2} \text{ atm}$ **29. a.** 642 torr, 0.845 atm, $8.56 \times 10^4 \text{ Pa}$; **b.** 975 torr; 1.28 atm; $1.30 \times 10^5 \text{ Pa}$; **c.** 517 torr; 850. torr **31.** 0.972 atm **33.** 44.8 L **35. a.** 14.0 L; **b.** $4.72 \times 10^{-2} \text{ mol}$; **c.** 678 K; **d.** 133 atm **37.** $4.44 \times 10^3 \text{ g He}$; $2.24 \times 10^3 \text{ g H}_2$ **39. a.** 69.6 K; **b.** 32.3 atm **41.** The balloon will burst **43.** 33.5 MPa **45.** $5.1 \times 10^4 \text{ torr}$ **47.** The volume of the balloon increases from 1.00 L to 2.82 L, so the change in volume is 1.82 L. **49.** 0.27 g **51.** 4.23 L O_2 ; 4.23 L CO_2 ; 4.23 L H_2O **53.** $1.5 \times 10^7 \text{ g Fe}$, $2.6 \times 10^7 \text{ g } 98\% \text{ H}_2\text{SO}_4$ **55.** 2.47 mol H_2O **57. a.** $2\text{CH}_4(\text{g}) + 2\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{HCN}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$; **b.** 13.3 L **59.** 42.1 g/mol, C_3H_6 **61.** 5.77 g/L (SiCl_4), 4.60 g/L (SiHCl_3) **63.** 1.1 atm, $P_{\text{CO}_2} = 1.1 \text{ atm}$, $P_{\text{TOTAL}} = 2.1 \text{ atm}$ **65.** $P_{\text{H}_2} = 317 \text{ torr}$, $P_{\text{N}_2} = 50.7 \text{ torr}$, $P_{\text{TOTAL}} = 368 \text{ torr}$ **67. a.** $\chi_{\text{CH}_4} = 0.412$, $\chi_{\text{O}_2} = 0.588$; **b.** 0.161 mol; **c.** 1.06 g CH_4 , 3.03 g O_2 **69.** 0.990 atm; 0.625 g

71. 18.0% 73. 3.40×10^3 J/mol (273 K); 6.81×10^3 J/mol (546 K)
 75. CH_4 : 652 m/s (273 K); 921 m/s (546 K); N_2 : 493 m/s (273 K); 697 m/s (546 K) 77. Both the average kinetic energy and the average velocity will increase with an increase in temperature. 79. a. All the same; b. Flask C 81. NO 83. The relative rates of effusion of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ are 1.04, 1.02, and 1.00. Advantage: CO_2 isn't as toxic as CO. Disadvantages: Can get a mixture of oxygen isotopes in CO_2 , so some species would effuse at about the same rate. 85. a. 12.24 atm; b. 12.13 atm; c. The ideal gas law is high by 0.91%. 87. 5×10^{-7} atm, 1×10^{13} molecules/cm³ 89. 0.4 mL 91. $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + \text{HNO}_2(\text{aq})$; $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$



95. MnCl_4 97. 1490 99. 24 torr 101. 4.1×10^6 L air; 7.42×10^5 L H_2
 103. 490 atm 105. $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ has a molar mass of 207 g/mol and $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$ had a molar mass of 311 g/mol. The molar mass calculated from the first data set is 209 g/mol and from the second data set is 202 g/mol. These experiment results are close to the expected value of 207 g/mol for $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$. Thus we conclude from these data that beryllium is a divalent element with an atomic mass of 9.0 amu. 107. 13.3% N 109. The pressure will increase initially because H_2 will effuse into container A faster than air will escape. However, the pressures will equalize once the gases have had time to mix thoroughly. 111. CO_2 113. 13.4% CaO , 86.6% BaO 115. a. 8.7×10^3 L air/min; b. $\chi_{\text{CO}} = 0.0017$, $\chi_{\text{CO}_2} = 0.032$, $\chi_{\text{O}_2} = 0.13$, $\chi_{\text{N}_2} = 0.77$, $\chi_{\text{H}_2\text{O}} = 0.067$ 117. a. 1.01×10^4 g; b. 6.65×10^4 g; c. 8.7×10^3 g 119. a. 0.19 torr; b. 6.6×10^{15} molecules CO/cm^3

Chapter 6

9. A coffee-cup calorimeter is at constant pressure. The heat at constant P equals ΔH . A bomb calorimeter is at constant volume. The heat at constant V equals ΔE . 11. Al. Al has a higher heat capacity and a lower density than Fe. The same amount of heat could be dissipated by a smaller mass of Al. 13. A function whose change depends only on the initial and final states and not on the pathway from the initial to the final state. If H

and E were not state functions, the law of conservation of energy (first law) would not be true. 15. Standard enthalpies of formation provide a reference point, allowing ΔH comparisons. 17. 150 J 19. 1.0 kg object with velocity of 2.0 m/s. 21. a. 36 kJ; b. 35 kJ; c. -85 kJ; d. all 23. -21 kJ 25. 10. L · atm = 1.0×10^3 J 27. $q = 30.9$ kJ, $w = -12.4$ kJ, $\Delta E = 18.5$ kJ 29. This is an endothermic reaction, so heat must be absorbed to convert reactants into products. The high-temperature environment of internal combustion engines provides the heat. 31. a. endothermic; b. exothermic; c. exothermic; d. endothermic 33. a. -1650 kJ; b. -826 kJ; c. -7.39 kJ; d. -34.4 kJ 35. 4400 g C_3H_8 37. $\text{H}_2\text{O}(\text{l})$; 2.30×10^3 J; $\text{Hg}(\text{l})$; 140°C 39. 0.129 J/g · °C, 26.7 J/mol · °C 41. 311 K 43. 0.25 J/g · °C 45. -66 kJ/mol 47. 39.2°C 49. 1.65 kJ/°C; -25.2 kJ/g; -3830 kJ/mol 51. -220.8 kJ 53. -58.0 kJ 55. -233 kJ 57. 28.4 kJ 59. The enthalpy change for the formation of one mole of a compound from its elements, with all substances in their standard states. $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$; $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$; $6\text{C}_{\text{graphite}}(\text{s}) + 6\text{H}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s})$; $\text{Pb}(\text{s}) + \text{S}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{PbSO}_4(\text{s})$ 61. a. -940. kJ; b. -265 kJ; c. -176 kJ 63. a. -908 kJ, -112 kJ, -140. kJ; b. $12\text{NH}_3(\text{g}) + 21\text{O}_2(\text{g}) \rightarrow 8\text{HNO}_3(\text{aq}) + 4\text{NO}(\text{g}) + 14\text{H}_2\text{O}(\text{g})$, exothermic 65. -2677 kJ 67. -169 kJ/mol 69. -29.67 kJ/g 71. For $\text{C}_3\text{H}_8(\text{g})$, -50.37 kJ/g vs. -47.7 kJ/g for octane. Because of the low boiling point of propane, there are extra safety hazards associated with using the necessary high-pressure compressed gas tanks. 73. 1.05×10^5 L 75. a. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; $w > 0$; b. $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$; $w < 0$; c. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$; $w = 0$; Compare the sum of the coefficients of all the product gases in the balanced equation to the sum of the coefficients of all the reactant gases. When a balanced reaction has more mol of product gases than mol of reactant gases, then the reaction will expand in volume (ΔV is positive) and the system does work on the surroundings ($w < 0$). When a balanced reaction has a decrease in the mol of gas from reactants to products, then the reaction will contract in volume (ΔV is negative) and the surroundings does compression work on the system ($w > 0$). When there is no change in the mol of gas from reactants to products, then $\Delta V = 0$ and $w = 0$. 77. 25 J 79. 75.0 g 81. -4.2 kJ 83. 25.91°C 85. a. 632 kJ; b. $\text{C}_2\text{H}_2(\text{g})$ 87. a. -361 kJ; b. -199 kJ; c. -227 kJ; d. -112 kJ 89. a. $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 12\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l})$; b. -5630 kJ; c. -5630 kJ 91. 37 m^2 93. 1×10^4 steps

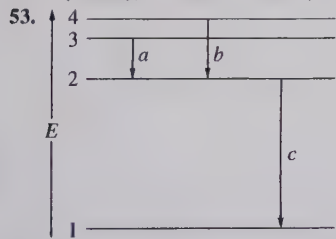
Chapter 7

15. Planck found it necessary to assume quantized energies to explain the radiation that heated bodies emit. Einstein's analysis of the photoelectric effect. 17. Only very small particles with a tiny mass exhibit wave and particle properties—for example, an electron. Some evidence supporting the wave properties of matter are (1) electrons can be diffracted like light and (2) the electron microscope uses electrons in a fashion similar to the way in which light is used in a light microscope. 19. n : gives the energy (it completely specifies the energy only for the H atom or ions with one electron) and the relative size of the orbitals; ℓ : gives the type (shape) of orbital; m_ℓ : gives information about the direction in which the orbital is pointing. 21. A surface where the probability of finding an electron is zero. 23. No, the spin is a convenient model. Since we cannot locate or "see" the electron, we cannot see if it is spinning. 25. The outermost electrons are the valence electrons. When atoms interact, the outermost electrons are involved in these interactions. In addition, how tightly the nucleus holds these outermost electrons determines atomic size, ionization energy, and other properties of atoms. Elements in the same group have similar valence electron configurations and, as a result, similar chemical properties. 27. Across a period, the positive charge from the nucleus increases as protons are added. The number of electrons also increases, but these outer electrons do not completely shield the increasing nuclear charge from each other. The general result is that the outer electrons are more

strongly held by the nucleus as one goes across a period, which results in larger ionization energies (and smaller size). Aluminum is out of order because the electrons in the filled 3s orbital shield some of the nuclear charge from the 3p electron. Hence, the 3p electron is less tightly bound than a 3s electron, resulting in a lower ionization energy for aluminum as compared to magnesium. The ionization energy of sulfur is lower than that of phosphorus because of the extra electron–electron repulsions in the doubly occupied sulfur 3p orbital. These added repulsions, which are not present in phosphorus, makes it slightly easier to remove an electron from sulfur as compared to phosphorus. **29.** $P(g) \rightarrow P^+(g) + e^-$; $P(g) + e^- \rightarrow P^-(g)$

31. The valence electrons are strongly attracted to the nucleus for elements with large ionization energies. One would expect these species to readily accept another electron and have very exothermic electron affinities. The noble gases are an exception; they have a large ionization energy but an endothermic electron affinity. Noble gases have a stable arrangement of electrons. Adding an electron disrupts this stable arrangement, resulting in unfavorable electron affinities. **33.** For hydrogen, all orbitals with the same value of n have the same energy. For polyatomic atoms/ions, the energy of the orbitals also depends on ℓ . Since there are more nondegenerate energy levels for polyatomic atoms/ions as compared with hydrogen, then there are many more possible electronic transitions resulting in more complicated line spectra. **35.** Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron–electron repulsions. **37.** Ionization energy applies to the removal of the electron from the atom in the gas phase. The work function applies to the removal of an electron from the solid. **39.** $3.84 \times 10^{14} \text{ s}^{-1}$

41. $3.0 \times 10^{10} \text{ s}^{-1}$, $2.0 \times 10^{-23} \text{ J/photon}$, 12 J/mol **43.** Wave a has the longer wavelength ($4.0 \times 10^{-4} \text{ m}$). Wave b has the higher frequency ($1.5 \times 10^{12} \text{ s}^{-1}$) and larger photon energy ($9.9 \times 10^{-22} \text{ J}$). Since both of these waves represent electromagnetic radiation, they should travel at the same speed, c , the speed of light. Both waves represent infrared radiation. **45.** 427.7 nm **47.** **a.** $1.5 \times 10^{-6} \text{ nm}$; **b.** $4.4 \times 10^{-25} \text{ nm}$ **49.** 2.4 nm **51.** **a.** 656.7 nm (visible); **b.** 486.4 nm (visible); **c.** 121.6 nm (ultraviolet)



53. **55.** $n = 1 \rightarrow n = 5$, $\lambda = 95.00 \text{ nm}$; $n = 2 \rightarrow n = 6$, $\lambda = 410.4 \text{ nm}$; visible light has sufficient energy for the $n = 2 \rightarrow n = 6$ transition but does not have sufficient energy for the $n = 1 \rightarrow n = 5$ transition. **57.** $n = 6$ **59.** **a.** $5.79 \times 10^{-4} \text{ m}$; **b.** $3.64 \times 10^{-33} \text{ m}$; **c.** The diameter of an H atom is roughly $1.0 \times 10^{-8} \text{ cm}$. The uncertainty in position is much larger than the size of the atom. **d.** The uncertainty is insignificant compared to the size of a baseball. **61.** $n = 1, 2, 3, \dots$; $\ell = 0, 1, 2, \dots (n - 1)$; $m_\ell = -\ell, \dots, -2, -1, 0, 1, 2, \dots, +\ell$. **63.** **b.** ℓ must be $< n$; **d.** For $\ell = 0$, $m_\ell = 0$ only **65.** ψ^2 gives the probability of finding the electron at that point. **67.** 3; 1; 5; 25; 16 **69.** **a.** 32; **b.** 8; **c.** 25; **d.** 10; **e.** 6 **71.** Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ or $[\text{Ne}] 3s^2 3p^2$; Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or $[\text{Ar}] 4s^2 3d^{10} 4p^1$; As: $[\text{Ar}] 4s^2 3d^{10} 4p^3$; Ge: $[\text{Ar}] 4s^2 3d^{10} 4p^2$; Al: $[\text{Ne}] 3s^2 3p^1$; Cd: $[\text{Kr}] 5s^2 4d^{10}$; S: $[\text{Ne}] 3s^2 3p^4$; Sc: $[\text{Ar}] 4s^2 3d^1 4p^4$ **73.** Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$; Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$; P: $1s^2 2s^2 2p^6 3s^2 3p^3$; Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$ (Actual: $[\text{Xe}] 6s^2 4f^{14} 5d^9$); Eu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$ (Actual: $[\text{Xe}] 6s^2 4f^{14} 5d^9$); Xe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$; Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$; **75.** Cr, Cu, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Pt, Au **77.** **a.** I: $[\text{Kr}] 5s^2 4d^{10} 5p^5$; **b.** element 120: $[\text{Rn}] 7s^2 5f^{14} 6d^{10} 7p^6 8s^2$; **c.** Rn: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^6$; **d.** Cr: $[\text{Ar}] 4s^1 3d^5$

79. B: $1s^2 2s^2 2p^1$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	$+\frac{1}{2}$
1s	1	0	0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
2s	2	0	0	$-\frac{1}{2}$
2p	2	1	-1	$+\frac{1}{2}$

N: $1s^2 2s^2 2p^3$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	$+\frac{1}{2}$
1s	1	0	0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
2s	2	0	0	$-\frac{1}{2}$
2p	2	1	-1	$+\frac{1}{2}$
2p	2	1	0	$+\frac{1}{2}$
2p	2	1	+1	$+\frac{1}{2}$

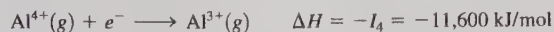
For boron, there are six possibilities for the 2p electron. For nitrogen, all the 2p electrons could have $m_s = -\frac{1}{2}$. **81.** none; an excited state; energy released **83.** Li (1 unpaired electron), N (3 unpaired electrons), Ni (2 unpaired electrons), and Te (2 unpaired electrons) are all expected to be paramagnetic because they have unpaired electrons. **85.** **a.** $\text{Be} < \text{Mg} < \text{Ca}$; **b.** $\text{Xe} < \text{I} < \text{Te}$; **c.** $\text{Ge} < \text{Ga} < \text{In}$ **87.** **a.** $\text{Ca} < \text{Mg} < \text{Be}$; **b.** $\text{Te} < \text{I} < \text{Xe}$; **c.** $\text{In} < \text{Ga} < \text{Ge}$ **89.** **a.** Li; **b.** P; **c.** O^+ ; **d.** Cl; **e.** Cu **91.** **a.** $[\text{Rn}] 7s^2 5f^{14} 6d^4$; **b.** W; **c.** Using Sg as a symbol for element 106, SgO_3 and SgO_4^{2-} probably would form (similar to Cr). **93.** Se is an exception to the general ionization trend. There are extra electron–electron repulsions in Se because two electrons are in the same 4p orbital, resulting in a lower ionization energy than expected. **95.** **a.** C, Br; **b.** N, Ar; **c.** C, Br **97.** **a.** $\text{Se} < \text{S}$; **b.** $\text{I} < \text{Br} < \text{F} < \text{Cl}$ **99.** Electron–electron repulsions are much greater in O^- than S^- because the electron goes into a smaller 2p orbital vs. the larger 3p orbital on sulfur, resulting in a more favorable (more exothermic) E.A. for sulfur. **101.** **a.** -1445 kJ/mol ; **b.** -580 kJ/mol **103.** potassium peroxide, K_2O_2 ; K^{2+} unstable **105.** $6.582 \times 10^{14} \text{ s}^{-1}$; $4.361 \times 10^{-19} \text{ J}$ **107.** Yes; the ionization energy general trend decreases down a group and the atomic radius trend increases down a group. The data in Table 7.8 confirm both of these general trends. **109.** **a.** $4\text{Li}(s) + \text{O}_2(g) \rightarrow 2\text{Li}_2\text{O}(s)$; **b.** $2\text{K}(s) + \text{S}(s) \rightarrow \text{K}_2\text{S}(s)$ **111.** 386 nm **113.** 200 s **115.** $\lambda = 4.104 \times 10^{-5} \text{ cm}$ so violet light is emitted. **117.** **a.** true for H only; **b.** true for all atoms; **c.** true for all atoms **119.** **a.** 20; **b.** 18; **c.** 10; **d.** 24 **121.** The element with the smallest first ionization energy (I_1) is Al (the green plot), the next highest I_1 belongs to Mg (the blue plot), and Si has the largest I_1 (the purple plot). Mg is the element with the huge jump between I_2 and I_3 ; it has two valence electrons so the third electron removed is an inner-core electron. Inner-core electrons are always much more difficult to remove as compared to valence electrons because they are closer to the nucleus, on average, as compared to the valence electrons. **123.** Valence electrons are easier to remove than inner-core electrons. The large difference in energy between I_2 and I_3 indicates that this element has two valence electrons. The element is most likely an alkaline earth metal because alkaline earth metals have two valence electrons. **125.** **a.** 146 kJ ; **b.** 407 kJ ; **c.** 1117 kJ ; **d.** 1524 kJ **127.** 4 **129.** For $r = a_0$ and $\theta = 0^\circ$, $\psi^2 = 2.46 \times 10^{28}$. For $r = a_0$ and $\theta = 90^\circ$, $\psi^2 = 0$. As expected, the xy plane is a node for the $2p_x$ atomic orbital.

131. a.

1							2
3							4
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

b. 2, 4, 12, and 20; **c.** There are many possibilities. One example of each formula is $\text{XY} = 1 + 11$, $\text{XY}_2 = 6 + 11$, $\text{X}_2\text{Y} = 1 + 10$, $\text{XY}_3 = 7 + 11$, and $\text{X}_2\text{Y}_3 = 7 + 10$; **d.** 6; **e.** 0; **f.** 18 **133.** **a.** As we remove succeeding electrons, the electron being removed is closer to the nucleus and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus and it takes more energy to remove these electrons. **b.** For I_4 , we begin removing an electron with $n = 2$. For I_3 , we

removed an electron with $n = 3$. In going from $n = 3$ to $n = 2$ there is a big jump in ionization energy because the $n = 2$ electrons (inner core) are much closer to the nucleus on the average than the $n = 3$ electrons (valence electrons). Since the $n = 2$ electrons are closer to the nucleus, they are held more tightly and require a much larger amount of energy to remove them. **c.** Al^{4+} ; the electron affinity for Al^{4+} is ΔH for the reaction



d. The greater the number of electrons, the greater the size. So

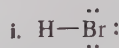
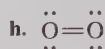
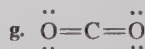
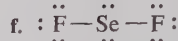
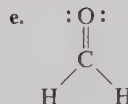
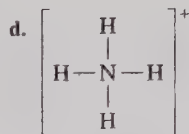
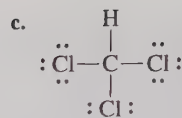
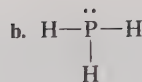
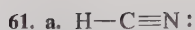


Chapter 8

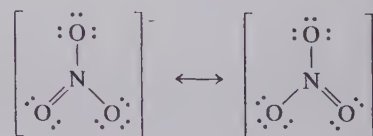
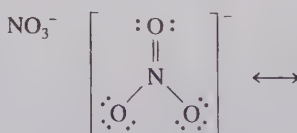
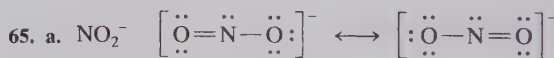
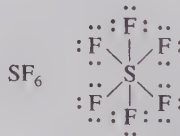
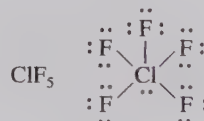
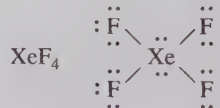
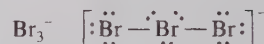
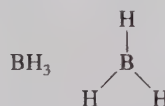
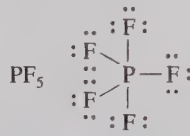
13. a. Electronegativity: the ability of an atom in a molecule to attract electrons to itself. Electron affinity: the energy change for $\text{M}(\text{g}) + \text{e}^- \rightarrow \text{M}^-(\text{g})$. Electron affinity deals with isolated atoms in the gas phase. **b.** Covalent bond: sharing of electron pair(s); polar covalent bond: unequal sharing of electron pair(s). **c.** Ionic bond: electrons are no longer shared, as in a covalent bond. Instead, there is a complete transfer of electron(s) from one atom to another to form ions. **15.** H_2O and NH_3 have lone pair electrons on the central atoms. These lone pair electrons require more space than the bonding electrons, which tends to compress the angles between the bonding pairs. The bond angle for H_2O is the smallest because oxygen has two lone pairs on the central atom and the bond angle is compressed more than in NH_3 , where N has only one lone pair. **17.** 1. polar bonds; 2. a structure such that the bond dipoles of the polar bonds do not cancel **19.** $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}_3(\text{PO}_4)_2$ are compounds with both ionic and covalent bonds **21. a.** $\text{C} < \text{N} < \text{O}$; **b.** $\text{Se} < \text{S} < \text{Cl}$; **c.** $\text{Sn} < \text{Ge} < \text{Si}$; **d.** $\text{Ti} < \text{Ge} < \text{S}$ **23. a.** $\text{Ge}-\text{F}$; **b.** $\text{P}-\text{Cl}$; **c.** $\text{S}-\text{F}$; **d.** $\text{Ti}-\text{Cl}$ **25.** Order of electronegativity from Fig. 8.3: **a.** $\text{C}(2.5) < \text{N}(3.0) < \text{O}(3.5)$, same; **b.** $\text{Se}(2.4) < \text{S}(2.5) < \text{Cl}(3.0)$, same; **c.** $\text{Si} = \text{Ge} = \text{Sn}(1.8)$, different; **d.** $\text{Ti}(1.8) = \text{Ge}(1.8) < \text{S}(2.5)$, different. Most polar bonds using actual electronegativity values: **a.** $\text{Si}-\text{F}$ and $\text{Ge}-\text{F}$ equal polarity ($\text{Ge}-\text{F}$ predicted); **b.** $\text{P}-\text{Cl}$ (same as predicted); **c.** $\text{S}-\text{F}$ (same as predicted); **d.** $\text{Ti}-\text{Cl}$ (same as predicted) **27.** $\text{F}-\text{H} > \text{O}-\text{H} > \text{N}-\text{H} > \text{C}-\text{H} > \text{P}-\text{H}$ **29.** Rb^+ and Se^{2-} : $[\text{Ar}]4s^23d^{10}4p^6$; Ba^{2+} and I^- : $[\text{Kr}]5s^24d^{10}5p^6$ **31. a.** Sc^{3+} ; **b.** Te^{2-} ; **c.** Ce^{4+} , Ti^{4+} ; **d.** Ba^{2+} **33.** Some possibilities are N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} , and Al^{3+} . $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$ **35. a.** $\text{Cu} > \text{Cu}^+ > \text{Cu}^{2+}$; **b.** $\text{Pt}^{2+} > \text{Pd}^{2+} > \text{Ni}^{2+}$; **c.** $\text{O}^{2-} > \text{O}^- > \text{O}$; **d.** $\text{La}^{3+} > \text{Eu}^{3+} > \text{Gd}^{3+} > \text{Yb}^{3+}$; **e.** $\text{Te}^{2-} > \text{I}^- > \text{Cs}^+ > \text{Ba}^{2+} > \text{La}^{3+}$ **37. a.** Li_3N (lithium nitride); **b.** Ga_2O_3 (gallium oxide); **c.** RbCl (rubidium chloride); **d.** BaS (barium sulfide) **39. a.** NaCl , Na^+ smaller than K^+ ; **b.** LiF , F^- smaller than Cl^- ; **c.** MgO , O^{2-} greater charge than OH^- ; **d.** $\text{Fe}(\text{OH})_3$, Fe^{3+} greater charge than Fe^{2+} ; **e.** Na_2O , O^{2-} greater charge than Cl^- ; **f.** MgO , Mg^{2+} smaller than Ba^{2+} , and O^{2-} smaller than S^{2-} . **41.** $\Delta H_f^\circ = -412 \text{ kJ/mol}$ **43.** The lattice energy for $\text{Mg}^{2+}\text{O}^{2-}$ will be much more exothermic than for Mg^+O^- . **45.** Ca^{2+} has greater charge than Na^+ , and Se^{2-} is smaller than Te^{2-} . Since charge differences affect lattice energy values more than size differences, we expect the trend from most exothermic to least exothermic to be:



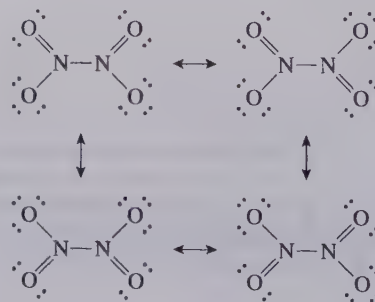
47. a. -183 kJ ; **b.** -109 kJ **49.** -42 kJ **51.** -1276 kJ **53.** 146 kJ/mol **55. a.** Using standard enthalpies of formation, $\Delta H^\circ = -184 \text{ kJ}$ vs. -183 kJ from bond energies; **b.** Using standard enthalpies of formation, $\Delta H = -92 \text{ kJ}$ vs. -109 kJ from bond energies. Bond energies give a reasonably good estimate for ΔH , especially when all reactants and products are gases. **57. a.** Using SF_4 data: $D_{\text{SF}} = 342.5 \text{ kJ/mol}$. Using SF_6 data: $D_{\text{SF}} = 327.0 \text{ kJ/mol}$. **b.** The $\text{S}-\text{F}$ bond energy in the table is 327 kJ/mol . The value in the table was based on the $\text{S}-\text{F}$ bond in SF_6 . **c.** $\text{S}(\text{g})$ and $\text{F}(\text{g})$ are not the most stable forms of the elements at 25°C . The most stable forms are $\text{S}_8(\text{s})$ and $\text{F}_2(\text{g})$; $\Delta H_f^\circ = 0$ for these two species. **59.** 388.2 kJ/mol vs. 391 kJ/mol in text



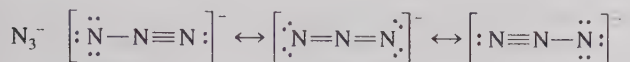
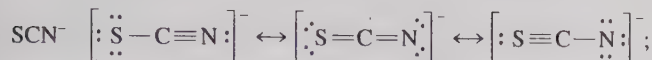
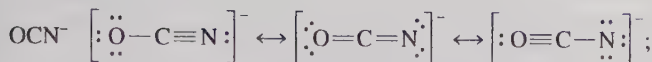
63.



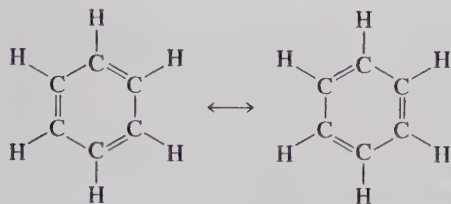
N_2O_4



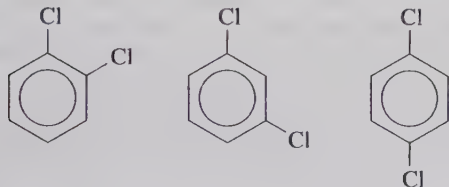
b.



67.



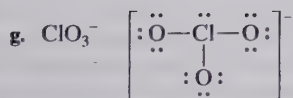
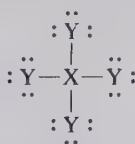
69. With resonance all carbon-carbon bonds are equivalent (we indicate this with a circle in the ring), giving three different structures:



Localized double bonds give four unique structures.

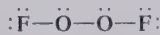
71. N_2 (triple bond) < N_2F_2 (double bond) < N_2F_4 (single bond)

73. a.-f. and h. all have similar Lewis structures:



Formal charges: a. +1; b. +2; c. +3; d. +1; e. +2; f. +4; g. +2; h. +1

75.

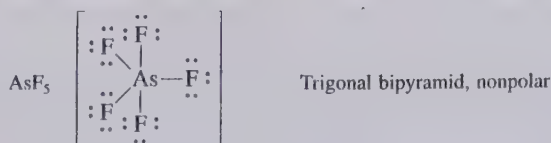
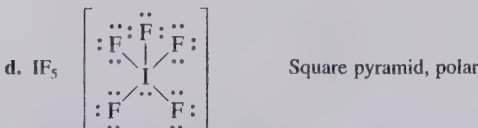
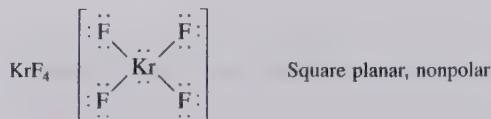
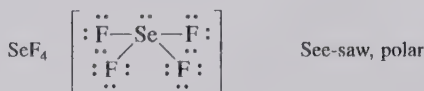
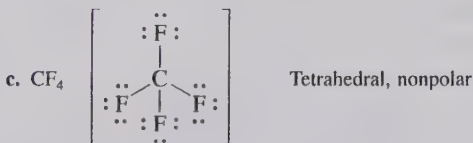
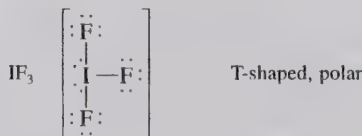
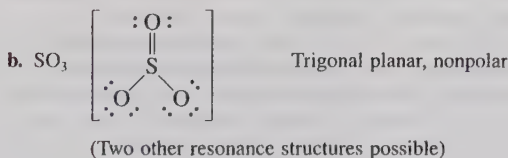
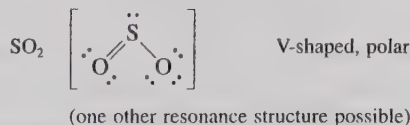
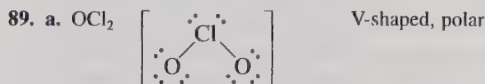


Formal charge: 0 0 0 0

Oxidation number: -1 +1 +1 -1

Oxidation numbers are more useful. We are forced to assign +1 as the oxidation number for oxygen. Oxygen is very electronegative and +1 is not a stable oxidation state for this element. 77. [61] a. linear, 180° ; b. trigonal pyramid, $<109.5^\circ$; c. tetrahedral, 109.5° ; d. tetrahedral, 109.5° ; e. trigonal planar, 120° ; f. V-shaped, $<109.5^\circ$; g. linear, 180° ; h. and i. linear, no bond angle in diatomic molecules; [65] a. NO_2^- : V-shaped, $\sim 120^\circ$; NO_3^- : trigonal planar, 120° ; N_2O_4 : trigonal planar about both N atoms, 120° ; b. all are linear, 180° 79. Br_3^- : linear; ClF_3 and BrF_3 : T-shaped; SF_4 : see-saw 81. a. trigonal planar; 120° ; b. V-shaped; $\sim 120^\circ$ 83. a. linear; 180° ; b. T-shaped; $\sim 90^\circ$; c. see-saw; $\sim 90^\circ$ and $\sim 120^\circ$; d. trigonal bipyramid; 90° and 120° 85. SeO_2 (bond dipoles do not cancel

each other out in SeO_2) 87. ICl_3 and TeF_4 (bond dipoles do not cancel each other out in ICl_3 and TeF_4)

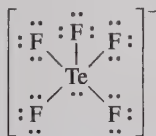


91. Element E is a halogen (F, Cl, Br, or I); trigonal pyramid; $<109.5^\circ$

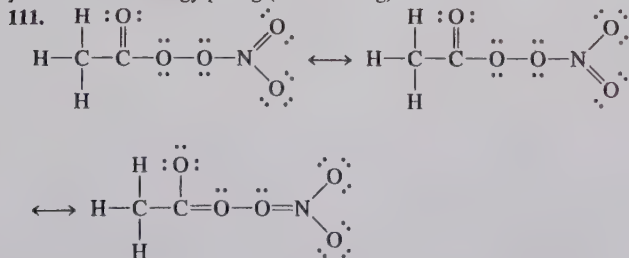
93. The polar bonds are symmetrically arranged about the central atoms, and all the individual bond dipoles cancel to give no net dipole moment

for each molecule, i.e., the molecules are nonpolar. **95. a.** radius: $N^+ < N < N^-$; I.E. $N^- < N < N^+$; **b.** radius: $Cl^+ < Cl < Cl^-$; I.E. $Se^- < Se < Cl < Cl^+$; **c.** radius: $Sr^{2+} < Rb^+ < Br^-$; I.E. $Br^- < Rb^+ < Sr^{2+}$; **97. a.** 1549 kJ; **b.** 1390. kJ **c.** 1312 kJ; **d.** 1599 kJ **99. a.** NaBr: In $NaBr_2$, the sodium ion would have a +2 charge assuming each bromine has a -1 charge. Sodium doesn't form stable Na^{2+} compounds. **b.** ClO_4^- : ClO_4 has 31 valence electrons so it is impossible to satisfy the octet rule for all atoms in ClO_4 . The extra electron from the -1 charge in ClO_4^- allows for complete octets for all atoms. **c.** XeO_4 : We can't draw a Lewis structure that obeys the octet rule for SO_4 (30 electrons), unlike XeO_4 (32 electrons). **d.** SeF_4 : Both compounds require the central atom to expand its octet. O is too small and doesn't have low-energy d orbitals to expand its octet (which is true for all row 2 elements). **101.** The general structure of the trihalide ions is $\left[\ddot{X}-\ddot{X}-\ddot{X} \right]^-$. Bromine and iodine

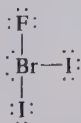
are large enough and have low-energy, empty d orbitals to accommodate the expanded octet. Fluorine is small and its valence shell contains only $2s$ and $2p$ orbitals (4 orbitals) and cannot expand its octet. The d orbitals in F are $3d$; they are too high in energy compared with $2s$ and $2p$ to be used. **103.** Yes, each structure has the same number of effective pairs around the central atom. (We count a multiple bond as a single group of electrons.) **105.**



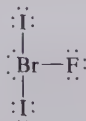
The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs. The stronger repulsion pushes the four square planar F atoms away from the lone pair, reducing the bond angles between the axial F atom and the square planar F atoms. **107.** As the halogen atoms get larger, it becomes more difficult to fit three halogen atoms around the small nitrogen atom, and the NX_3 molecule becomes less stable. **109.** reaction i: -2636 kJ; reaction ii: -3471 kJ; reaction iii: -3543 kJ; Reaction iii yields the most energy per kg (-8085 kJ/kg)



113. a. Two possible structures exist; each has a T-shaped molecular structure:

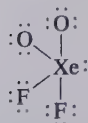


90° bond angle between I atoms

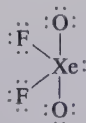


180° bond angle between I atoms

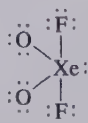
b. Three possible structures exist; each has a see-saw molecular structure.



90° bond angle
between O atoms

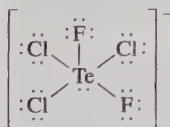


180° bond angle
between O atoms

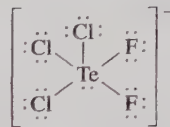


120° bond angle
between O atoms

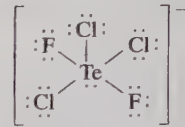
c. Three possible structures exist; each has a square pyramidal molecular structure.



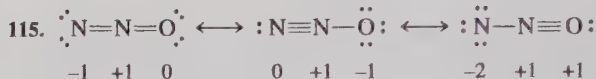
One F atom is 180°
from lone pair.



Both F atoms are 90°
from lone pair and 90°
from each other.



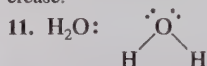
Both F atoms are 90°
from lone pair and 180°
from each other.



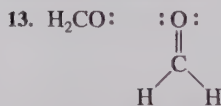
We should eliminate $N-N \equiv O$, since it has a formal charge of +1 on the most electronegative element (O). This is consistent with the observation that the N—N bond is between a double and triple bond and that the N—O bond is between a single and double bond.

Chapter 9

7. Bond energy is proportional to bond order. Bond length is inversely proportional to bond order. Bond energy and length can be measured. **9.** Paramagnetic: Unpaired electrons are present. Measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. Greater numbers of unpaired electrons will give greater attraction and greater observed mass increase.



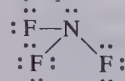
H_2O has a tetrahedral arrangement of the electron pairs about the O atom that requires sp^3 hybridization. Two of the sp^3 hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two sp^3 hybrid orbitals hold the two lone pairs on oxygen.



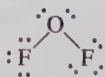
The central carbon atom has a trigonal planar arrangement of the electron pairs that requires sp^2 hybridization. Two of the sp^2 hybrid orbitals are used to form the two bonds to hydrogen. The other sp^2 hybrid orbital forms the σ bond to oxygen. The unchanged (unhybridized) p orbital on carbon is used to form the π bond between carbon and oxygen. **15. [61] a.** sp ; **b.** sp^3 ; **c.** sp^3 ; **d.** sp^3 ; **e.** sp^2 ; **f.** sp^3 ; **g.** sp ; **h.** each O is sp^2 hybridized; **i.** Br is sp^3 hybridized [65] **a.** NO_2^- , sp^2 ; NO_3^- , sp^2 ; N_2O_4 : both N atoms are sp^2 hybridized; **b.** All are sp hybridized. **17.** PF_5 , dsp^3 ; BeH_2 , sp ; BH_3 , sp^2 ; Br_3^- , dsp^3 ; SF_4 , dsp^3 ; XeF_4 , d^2sp^3 ; ClF_5 , d^2sp^3 ; SF_6 , d^2sp^3 **19.** The molecules in Exercise 81 all exhibit sp^2 hybridization about the central atom; the molecules in Exercise 82 all exhibit sp^3 hybridization about the central atom. **21. a.** tetrahedral, 109.5°, sp^3 , nonpolar



b. trigonal pyramidal, <109.5°, sp^3 , polar



- c. V-shaped, $<109.5^\circ$, sp^3 , polar



- d. trigonal planar, 120° , sp^2 , nonpolar



- e. linear, 180° , sp , nonpolar



- f. $a \approx 120^\circ$, see-saw, dsp^3 , polar
 $b \approx 90^\circ$

- g. $a = 90^\circ$, trigonal bipyramid, dsp^3 , nonpolar
 $b = 120^\circ$

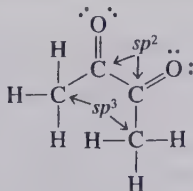
- h. linear, 180° , dsp^3 , nonpolar

- i. square planar, 90° , d^2sp^3 , nonpolar

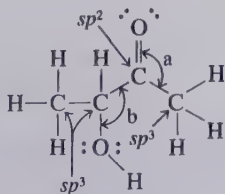
- j. octahedral, 90° , d^2sp^3 , nonpolar

- k. square pyramid, $\approx 90^\circ$, d^2sp^3 , polar
l. T-shaped, $\approx 90^\circ$, dsp^3 , polar

23. The π bond forces all six atoms into the same plane. 25. Biacetyl

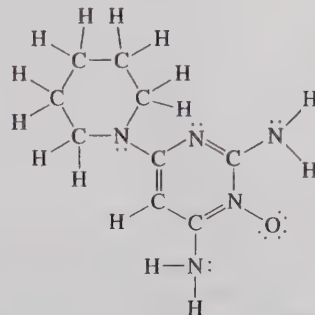


All CCO angles are 120° . The six atoms are not in the same plane. 11σ and 2π
Acetoin

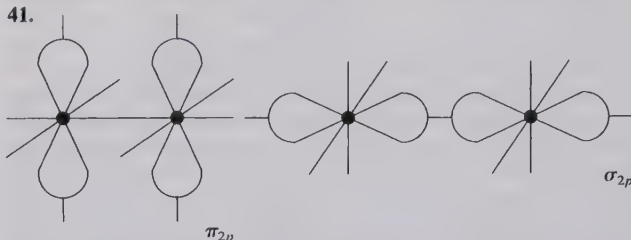


angle $a = 120^\circ$, angle $b = 109.5^\circ$, 13σ and 1π bond 27. To complete the Lewis structure, add lone pairs to complete octets for each atom. a. 6; b. 4; c. The center N in —N=N=N group; d. 33σ ; e. 5π ; f. 180° ; g. $<109.5^\circ$; h. sp^3

29.



- a. The two nitrogens in the ring with double bonds are sp^2 hybridized. The other three nitrogens are sp^3 hybridized. b. The five carbon atoms in the ring with one nitrogen are all sp^3 hybridized. The four carbon atoms in the other ring with double bonds are all sp^2 hybridized. c. Angles a and b : $\approx 109.5^\circ$; angles c , d , and e : $\approx 120^\circ$; d. 31σ bonds; e. 3π bonds 31. a. H_2^+ , H_2 , H_2^- ; b. He_2^{2+} and He_2^+ 33. a. $(\sigma_{2s})^2$, B.O. = 1; diamagnetic (0 unpaired electrons); b. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$, B.O. = 2; diamagnetic (0 unpaired electrons); c. $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$, B.O. = 2; paramagnetic (2 unpaired electrons) 35. O_2^+ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$, B.O. = 2.5; 1 unpaired electron; O_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$, B.O. = 2; 2 unpaired electrons; O_2^- : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$, B.O. = 1.5; 1 unpaired electron; O_2^{2-} : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$, B.O. = 1; 0 unpaired electrons; bond energy: $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+ < \text{O}_2^{2+}$; bond length: $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$ 37. a. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$, B.O. = 3; diamagnetic; b. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$, B.O. = 2.5; paramagnetic; c. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$, B.O. = 2; diamagnetic; bond length: $\text{CO} < \text{CO}^+ < \text{CO}^{2+}$; bond energy: $\text{CO}^{2+} < \text{CO}^+ < \text{CO}$ 39. H_2 , N_2

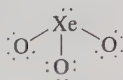


43. a. The electrons would be closer to F on the average. The F atom is more electronegative than the H atom, and the $2p$ orbital of F is lower in energy than the $1s$ orbital of H; b. The bonding MO would have more fluorine $2p$ character because it is closer in energy to the fluorine $2p$ orbital; c. The antibonding MO would place more electron density closer to H and would have a greater contribution from the higher-energy hydrogen $1s$ atomic orbital. 45. O_3 and NO_2^- have identical Lewis structures, so we need to discuss only one of them. The Lewis structure for O_3 is

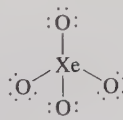


Localized electron model: The central oxygen atom is sp^2 hybridized, which is used to form the two σ bonds and hold the lone pair of electrons. An unchanged (unhybridized) p atomic orbital forms the π bond with the neighboring oxygen atoms. The π bond resonates between the two positions. Molecular orbital model: There are two localized σ bonds and a π bond that is delocalized over the entire surface of the molecule. The delocalized π bond results from overlap of a p atomic orbital on each oxygen atom in O_3 .

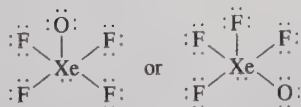
47. a. Trigonal pyramid; sp^3



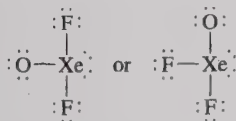
b. Tetrahedral; sp^3



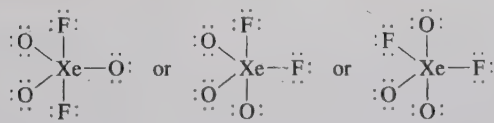
c. See-saw; dsp^3



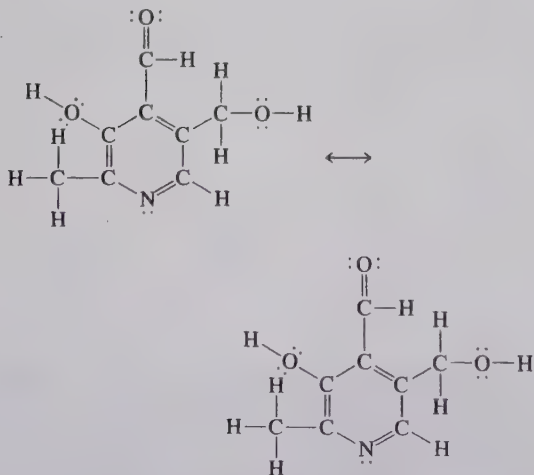
d. T-shaped; dsp^3



e. Trigonal bipyramid; dsp^3

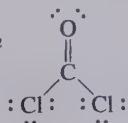


49.



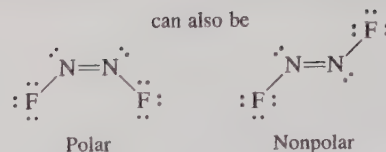
a. 20 σ bonds; 4 π bonds (The electrons in the 3 π bonds in the ring are delocalized.) b. angles a, c, and g: $\approx 109.5^\circ$; angles b, d, e, and f: $\approx 120^\circ$; c. 6 sp^2 carbons; d. 4 sp^3 atoms; e. Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp^2 hybridized. This leaves a p orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these p orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Fig. 9.48 of the text).

51. a. COCl_2



Trigonal planar, polar, 120° , sp^2

b. N_2F_2



V-shaped about both N atoms, $\approx 120^\circ$, sp^2

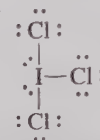
These are distinctly different molecules.

c. COS



Linear, polar, 180° , sp

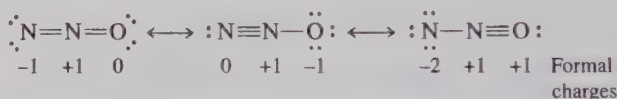
d. ICl_3



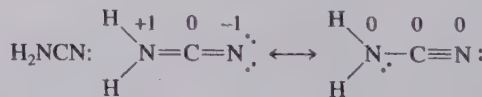
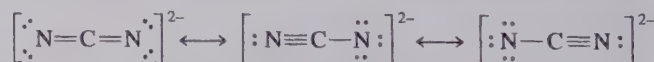
T-shaped, polar, $\approx 90^\circ$, dsp^3

53. a. The NNO structure is correct. From the Lewis structures we would predict both NNO and NON to be linear, but NON would be nonpolar. NNO is polar.

b.

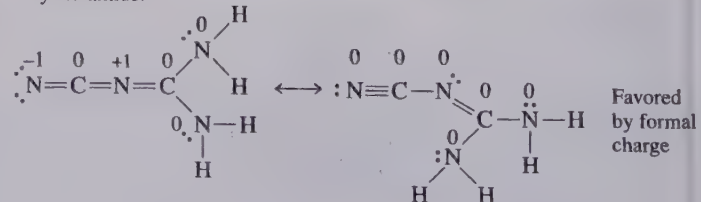


The central N is sp hybridized. We can probably ignore the third resonance structure on the basis of formal charge. c. sp hybrid orbitals on the center N overlap with atomic orbitals (or hybrid orbitals) on the other two atoms to form two σ bonds. The remaining p orbitals on the center N overlap with p orbitals on the other N to form two π bonds. 55. N_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ in ground state, B.O. = 3, diamagnetic; 1st excited state: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}^*)^1$, B.O. = 2, paramagnetic (two unpaired electrons) 57. F_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$; F_2 should have a lower ionization energy than F. The electron removed from F_2 is in a π_{2p}^* antibonding molecular orbital, which is higher in energy than the $2p$ atomic orbitals from which the electron in atomic fluorine is removed. Since the electron removed from F_2 is higher in energy than the electron removed from F, then it should be easier to remove an electron from F_2 than from F. 59. a. No, some atoms are attached differently; b. Structure 1: All N = sp^3 , all C = sp^2 ; structure 2: All C and N = sp^2 ; c. The first structure with the carbon-oxygen double bonds is slightly more stable. 61. a. NCN^{2-} :



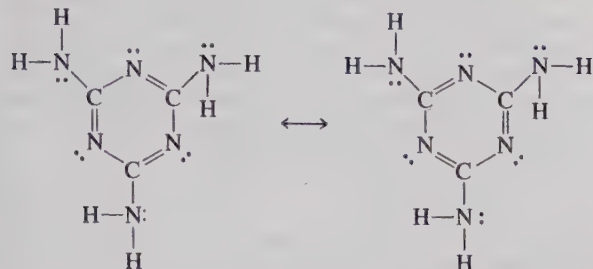
Favored by formal charge

Dicyandiamide:

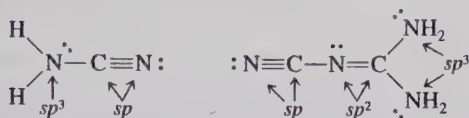


Favored by formal charge

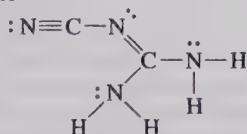
Melamine:



b. NCN^{2-} : C is sp hybridized. Cannot predict hybrids for N's (different for each resonance structure). For the remaining compounds, we will predict hybrids for the favored resonance structures only.



Melamine: N in NH_2 groups are all sp^3 hybridized. Atoms in ring are all sp^2 hybridized; **c.** NCN^{2-} : 2 σ and 2 π bonds; H_2NCN : 4 σ and 2 π bonds; dicyandiamide: 9 σ and 3 π bonds; melamine: 15 σ and 3 π bonds; **d.** The π system forces the ring to be planar just as the benzene ring is planar. **e.** The structure



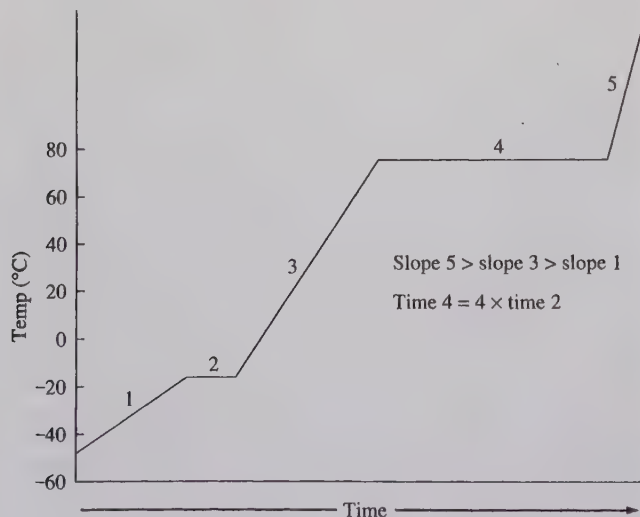
is the most important because it has three different CN bonds. This structure is also favored on the basis of formal charge. **63. a.** 25-nm light has sufficient energy to ionize N and N_2 and to break the triple bond in N_2 . Thus, N_2 , N_2^+ , N, and N^+ will all be present, assuming excess N_2 . **b.** 85.33 nm $< \lambda \leq 127$ nm; **c.** The ionization energy of a substance is the energy it takes to completely remove an electron. N_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; the electron removed from N_2 is in the σ_{2p} molecular orbital, which is lower in energy than the $2p$ atomic orbital from which the electron in atomic nitrogen is removed. Since the electron removed from N_2 is lower in energy than the electron removed in N, then the ionization energy of N_2 is greater than the ionization energy of N. **65.** Both reactions apparently involve only the breaking of the N—Cl bond. However, in the reaction $\text{ONCl} \rightarrow \text{NO} + \text{Cl}$ some energy is released in forming the stronger NO bond, lowering the value of ΔH . Therefore, the apparent N—Cl bond energy is artificially low for this reaction. The first reaction involves only the breaking of the N—Cl bond. **67. a.** The CO bond is polar, with the negative end around the more electronegative oxygen atom. We would expect metal cations to be attracted to and to bond to the oxygen end of CO on the basis of electronegativity. **b.** The formal charge on C is -1 , and the formal charge on O is $+1$. From formal charge, we would expect metal cations to bond to the carbon (with the negative formal charge.) **c.** In molecular orbital theory, only orbitals with proper symmetry overlap to form bonding orbitals. The metals that form bonds to CO are usually transition metals, all of which have outer electrons in the d orbitals. The only molecular orbitals of CO that have proper symmetry to overlap with d orbitals are the π_{2p}^* orbitals, whose shape is similar to that of the d orbitals (see Fig. 9.34). Since the antibonding molecular orbitals have more carbon character, one would expect the bond to form through carbon.

Chapter 10

13. London dispersion forces (LD forces) $<$ dipole–dipole $<$ H bonding $<$ metallic bonding, covalent network, ionic. Yes, there is considerable overlap. Consider some of the examples in Exercise 10.92. Benzene (only

LD forces) has a higher boiling point than acetone (dipole–dipole). Also, there is even more overlap of the stronger forces (metallic, covalent, and ionic). **15. a.** Polarizability of an atom refers to the ease of distorting the electron cloud. It also can refer to distorting the electron clouds in molecules or ions. **b.** London dispersion forces are present in all substances. LDF can be referred to as accidental dipole-induced dipole forces. Dipole–dipole forces involve the attraction of molecules with permanent dipoles for each other. **c. inter:** between; **intra:** within. For example, in Br_2 the covalent bond is an intramolecular force, holding the two Br atoms together in the molecule. The much weaker London dispersion forces are intermolecular forces of attraction, which hold different Br_2 molecules together in the liquid phase. **17.** Atoms have an approximately spherical shape. It is impossible to pack spheres together without some empty space between the spheres. **19.** As the intermolecular forces increase, the critical temperature increases. **21. a.** crystalline solid: long range order; amorphous solid: no long range order; **b.** ionic solid: contains ions held together by ionic bonding; molecular solid: contains discrete covalently bonded molecules held together in the solid by weaker forces (LDF, dipole, or hydrogen bonds); **c.** molecular solid: discrete molecules; covalent network solid: no discrete molecules. A covalent network is like a giant molecule. The intermolecular forces are the covalent bonds between the atoms. **d.** metallic solid: contains delocalized electrons; excellent conductor of electricity; covalent network: localized electrons, insulator or semiconductor **23. Conductor:** The energy difference between the filled and unfilled molecular orbitals is minimal. We call this energy difference the band gap. Since the band gap is minimal, electrons can easily move into the conduction bands (the unfilled molecular orbitals). **Insulator:** Large band gap. Electrons do not move from the filled molecular orbitals to the conduction bands since the energy difference is large. **Semiconductor:** Small band gap. Since the energy difference between the filled and unfilled molecular orbitals is smaller than in insulators, some electrons can jump into the conduction bands. The band gap, is not as small as with conductors, so semiconductors have intermediate conductivity. **a.** As the temperature is increased, more electrons in the filled molecular orbitals have sufficient kinetic energy to jump into the conduction bands (the unfilled molecular orbitals). **b.** A photon of light is absorbed by an electron, which then has sufficient energy to jump into the conduction bands. **c.** An impurity either adds electrons at an energy near that of the conduction bands (n-type) or creates holes (unfilled energy levels) at energies in the previously filled molecular orbitals (p-type). **25.** Ge doped with P or As would produce an n-type semiconductor, and Ge doped with Ga or In would produce a p-type semiconductor. **27. a.** condensation: vapor $\rightarrow$ liquid; **b.** evaporation: liquid $\rightarrow$ vapor; **c.** sublimation: solid $\rightarrow$ vapor; **d.** A supercooled liquid is a liquid at a temperature below its freezing point. **29. a.** As intermolecular forces increase, the rate of evaporation decreases. **b.** increase T : increase rate; **c.** increase surface area: increase rate **31.** $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{C}_2\text{H}_5\text{OH}(g)$ is an endothermic process. Heat is absorbed when liquid ethanol vaporizes; the internal heat from the body provides this heat. **33.** The phase change, $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ releases heat that can cause additional damage. Also steam can be at a temperature much greater than 100°C . **35. a.** LD (London dispersion); **b.** dipole, LD; **c.** hydrogen bonding, LD; **d.** ionic; **e.** LD; **f.** dipole, LD; **g.** ionic **37. a.** OCS ; **b.** SO_2 ; **c.** $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; **d.** H_2CO ; **e.** CH_3OH **39. a.** HCl has dipole forces in addition to LD forces; **b.** NaCl , stronger ionic forces; **c.** I_2 , larger molecule so stronger LD forces; **d.** N_2 , smallest nonpolar compound present, has weakest LD forces; **e.** CH_4 , smallest nonpolar compound present, has weakest LD forces; **f.** HF , can form relatively strong hydrogen bonding interactions, unlike the other compounds; **g.** $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, unlike others, has relatively strong hydrogen bonding. **41.** H_2O is attracted to glass while Hg is not. **43.** The structure of H_2O_2 produces greater hydrogen bonding than water. Long chains of hydrogen bonded H_2O_2 molecules then get tangled together. **45.** 3.13 Å **47.** 1.54

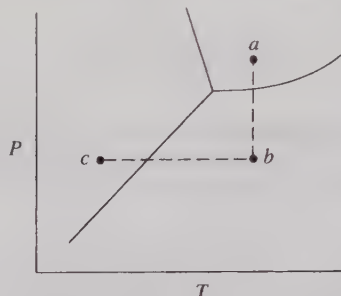
g/cm³ 49. 22.68 g/cm³ 51. edge, 328 pm; radius, 142 pm 53. For a cubic closest packed structure, 74.06% of the volume of each unit cell is occupied by atoms; in a simple cubic unit cell structure, 52.36% is occupied. The cubic (and hexagonal) closest packed structures provide the most efficient means for packing atoms. 55. p-type 57. 5.0×10^2 nm 59. NaCl: 4Na⁺, 4Cl⁻; CsCl: 1Cs⁺, 1Cl⁻; ZnS: 4Zn²⁺, 4S²⁻; TiO₂: 2Ti⁴⁺, 4O²⁻ 61. CoF₂ 63. MF₂ 65. From density data, 421 pm; from ionic radii data, 410. pm; the two values agree within 3%. 67. a. CO₂: molecular; b. SiO₂: covalent network; c. Si: atomic, covalent network; d. CH₄: molecular; e. Ru: atomic, metallic; f. I₂: molecular; g. KBr: ionic; h. H₂O: molecular; i. NaOH: ionic; j. U: atomic, metallic; k. CaCO₃: ionic; l. PH₃: molecular 69. a. The unit cell consists of Ni at the cube corners and Ti at the body center or Ti at the cube corners and Ni at the body center. b. NiTi; c. Both have a coordination number of 8. 71. CaTiO₃; six oxygens around each Ti 73. a. YBa₂Cu₃O₇; b. The structure of this superconductor material is based on the second perovskite structure. The YBa₂Cu₃O₇ structure is three of these cubic perovskite unit cells stacked on top of each other. The oxygen atoms are in the same places, Cu takes the place of Ti, and two Ca atoms are replaced by Ba and one Ca atom is replaced by Y. c. YBa₂Cu₃O₇ 75. Li, 158 kJ/mol; Mg, 139 kJ/mol. Bonding is stronger in Li. 77. 89°C 79. 2.56×10^{-3} torr 81.



83. 1680 kJ 85. 1490 g 87. A: solid; B: liquid; C: vapor; D: solid + vapor; E: solid + liquid + vapor (triple point); F: liquid + vapor; G: liquid + vapor (critical point); H: vapor; the first dashed line (at the lower temperature) is the normal melting point, and the second dashed line is the normal boiling point. The solid phase is denser. 89. a. two; b. higher pressure triple point: graphite, diamond, and liquid; lower pressure triple point: graphite, liquid and vapor; c. It is converted to diamond (the more dense solid form); d. Diamond is more dense, which is why graphite can be converted to diamond by applying pressure. 91. C₂₅H₅₂ has the stronger intermolecular forces because it has the higher boiling point. Even though C₂₅H₅₂ is nonpolar, it is so large that its London dispersion forces are much stronger than the sum of the London dispersion forces and hydrogen bonding interactions found in H₂O. 93. A: CH₄; B: SiH₄; C: NH₃ 95. 0.229 nm 97. If TiO₂ conducts electricity as a liquid, then it would be ionic. 99. B₂H₆, molecular; SiO₂, network; CsI, ionic; W, metallic 101. 4.65 kg/h 103. 46.7 kJ/mol; 90% 105. The solids with high melting points (NaCl, MgCl₂, NaF, MgF₂, AlF₃) are all ionic solids. SiCl₄, SiF₄, Cl₂, F₂, PF₅, and SF₆ are nonpolar covalent molecules with LD

forces. PCl₃ and SCl₂ are polar molecules with LD and dipole forces. In these 8 molecular substances the intermolecular forces are weak and the melting points low. AlCl₃ is intermediate. The melting point indicates there are stronger forces present than in the nonmetal halides, but not as strong as for an ionic solid. AlCl₃ illustrates a gradual transition from ionic to covalent bonding; from an ionic solid to discrete molecules. 107. TiO_{1.182} or Ti_{0.8462}O; 63.7% Ti²⁺, 36.3% Ti³⁺ 109. 6.58 g/cm³

111.



As P is lowered, we go from a to b on the phase diagram. The water boils. The evaporation of the water is endothermic and the water is cooled ($b \rightarrow c$), forming some ice. If the pump is left on, the ice will sublime until none is left. This is the basis of freeze drying.

Chapter 11

9. 0.365 M 11. 1.54×10^{-2} M NiCl₂, Ni²⁺: 1.54×10^{-2} M; Cl⁻: 3.08×10^{-2} M 13. Since volume is temperature-dependent and mass is not, then molarity is temperature-dependent and molality is temperature-independent. In determining ΔT_f and ΔT_b , we are interested in how some temperature depends on composition. Thus we do not want our expression of composition to also be dependent on temperature. 15. Hydrophobic: water hating; hydrophilic: water loving 17. The levels of the liquids in each beaker will become constant when the concentration of solute is the same in both beakers. Since A is less volatile, the beaker on the right will have a larger volume when the concentrations become equal. Water will initially condense in this beaker in a larger amount than solute is evaporating, while the net change occurring initially in the other beaker is for water to evaporate in a larger amount than solute is condensing. Eventually the rate that solute and H₂O leave and return to each beaker will become equal when the concentrations become equal. 19. No. For an ideal solution, $\Delta H_{\text{soln}} = 0$ 21. The osmotic pressure inside bacteria cells is less than outside the cell causing the cells to dehydrate and die. 23. The Tyndall effect is the scattering of light by particles. Colloids scatter light, and true solutions do not scatter light. 25. 2.5%; 0.43 M; 0.44 m; 7.9×10^{-3} 27. HCl: 12 M, 17 m, 0.23; HNO₃: 16 M, 37 m, 0.39; H₂SO₄: 18 M, 200 m, 0.76; HC₂H₃O₂: 17 M, 2000 m, 0.96; NH₃: 15 M, 23 m, 0.29 29. 35%; 0.39; 7.3 m; 3.1 M 31. 23.9%; 1.6 m, 0.028, 4.11 N 33. NaI(s) $\rightarrow$ Na⁺(aq) + I⁻(aq) $\Delta H_{\text{soln}} = -8$ kJ/mol 35. The attraction of water molecules for Al³⁺ and OH⁻ cannot overcome the larger lattice energy of Al(OH)₃. 37. Water will dissolve polar solutes (c and d) and ionic solutes (b). Carbon tetrachloride will dissolve nonpolar solutes (a and e). 39. Ability to form hydrogen bonding interactions, ability to break up into ions, and polarity are some factors affecting solute solubility. a. CH₃CH₂OH; b. CHCl₃; c. CH₃CH₂OH 41. As the length of the hydrocarbon chain increases, the solubility decreases because the nonpolar hydrocarbon chain interacts poorly with the polar water molecules. 43. 1.04×10^{-3} mol/L · atm; 1.14×10^{-3} mol/L 45. 23.6 torr 47. 3.0×10^2 g/mol 49. a. 290 torr; b. 0.69 51. $X_{\text{methanol}} = X_{\text{propanol}} = 0.500$ 53. solution c 55. $P_{\text{ideal}} = 188.6$ torr; $X_{\text{acetone}} = 0.512$, $X_{\text{methanol}} = 0.488$; since the actual vapor pressure of the solution is smaller than the ideal vapor pressure, then this solution exhibits a negative deviation from Raoult's law. This occurs when solute-solvent attractions are stronger than for the pure substances. 57. 100.042°C 59. 14.8 g C₃H₈O₃ 61. $T_f = -29.9^\circ\text{C}$, $T_b = 108.2^\circ\text{C}$

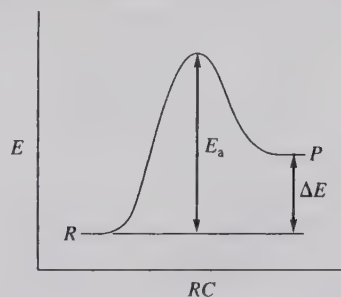
63. 456 g/mol 65. a. $\Delta T = 2.0 \times 10^{-5}^\circ\text{C}$, $\pi = 0.20$ torr; b. Osmotic pressure is better for determining the molar mass of large molecules. A temperature change of 10^{-5}°C is very difficult to measure. A change in height of a column of mercury by 0.2 mm is not as hard to measure precisely. 67. 0.327 M 69. a. 0.010 M Na_3PO_4 and 0.020 M KCl ; b. 0.020 M HF ; c. 0.020 M CaBr_2 71. a. $T_f = -0.28^\circ\text{C}$; $T_b = 100.077^\circ\text{C}$; b. $T_f = -0.37^\circ\text{C}$; $T_b = 100.10^\circ\text{C}$ 73. 2.63 (0.0225 m), 2.60 (0.0910 m), 2.57 (0.278 m); $i_{\text{average}} = 2.60$ 75. 37 atm; the osmotic pressure should be lower due to ion pairing. 77. a. 26.6 kJ/mol; b. -657 kJ/mol 79. a. Water boils when the vapor pressure equals the pressure above the water. In an open pan, $P_{\text{atm}} \approx 1.0$ atm. In a pressure cooker, $P_{\text{inside}} > 1.0$ atm and water boils at a higher temperature. The higher the cooking temperature, the faster the cooking time. b. Salt dissolves in water, forming a solution with a melting point lower than that of pure water ($\Delta T_f = K_f m$). This happens in water on the surface of ice. If it is not too cold, the ice melts. This process won't occur if the ambient temperature is lower than the depressed freezing point of the salt solution. c. When water freezes from a solution, it freezes as pure water, leaving behind a more concentrated salt solution. d. On the CO_2 phase diagram, the triple point is above 1 atm and $\text{CO}_2(\text{g})$ is the stable phase at 1 atm and room temperature. $\text{CO}_2(\text{l})$ can't exist at normal atmospheric pressures, which explains why dry ice sublimates rather than boils. In a fire extinguisher, $P > 1$ atm and $\text{CO}_2(\text{l})$ can exist. When CO_2 is released from the fire extinguisher, $\text{CO}_2(\text{g})$ forms as predicted from the phase diagram. e. Adding a solute to a solvent increases the boiling point and decreases the freezing point of the solvent. Thus, the solvent is a liquid over a wider range of temperatures when a solute is dissolved. 81. 0.600 83. $\text{C}_2\text{H}_4\text{O}_3$; 151 g/mol (exp.); 152.10 g/mol (calc.); $\text{C}_4\text{H}_8\text{O}_6$ 85. 1.97% NaCl 87. 0.050 89. 44% naphthalene, 56% anthracene 91. -0.20°C , 100.056°C 93. a. 46 L; b. No; A reverse osmosis system that applies 8.0 atm can purify only water with solute concentrations less than 0.32 mol/L. Salt water has a solute concentration of 2(0.60 M) = 1.2 M ions. The solute concentration of salt water is much too high for this reverse osmosis unit to work.

Chapter 12

9. For a generic reaction $A \rightarrow B$, an instantaneous rate is the slope of a tangent line to the graph of $[A]$ versus time (or $[B]$ versus time). We can determine an instantaneous rate at any time. The instantaneous rate at $t \approx 0$ is called the *initial rate*. Since a tangent line generally has the greatest slope at $t \approx 0$ versus tangent lines at other times, then the initial rate would have the largest rate value. The average rate is the change in concentration of a reactant or product per some time period ($\Delta[A]/\Delta t$); an average rate is determined over some time period while an instantaneous rate is determined at one specific time. 11. a. The greater the frequency of collisions, the greater the opportunity for molecules to react, and hence the greater the rate. b. Chemical reactions involve the making and breaking of chemical bonds. The kinetic energy of the collisions can be used to break bonds. So, as the kinetic energy of the collisions increases, the rate increases. c. For a reaction to occur, it is the reactive portion of each molecule that must be involved in a collision. Only some of all the possible collisions have the correct orientation to convert from reactants to products. 13. A catalyst increases the rate of a reaction by providing reactants with an alternate pathway (mechanism) to convert to products. This alternate pathway has a lower activation energy, increasing the rate of reaction. A homogeneous catalyst is in the same phase as the reactants. A heterogeneous catalyst is in a different phase than the reactants. The catalyst is usually a solid, although a catalyst in a liquid phase can act as a heterogeneous catalyst for some gas-phase reactions. No, the catalyzed reaction has a different mechanism and hence, most likely, a different rate law. 15. a. They are independent of each other. b. The rate law can be determined only from experiment. c. Most reactions occur by a multiple series of steps. 17. P_4 : 6.0×10^{-4} mol/L $\cdot$ s; H_2 : 3.6×10^{-3} mol/L $\cdot$ s 19. a. mol/L $\cdot$ s;

b. mol/L $\cdot$ s; c. s^{-1} ; d. L/mol $\cdot$ s; e. $\text{L}^2/\text{mol}^2 \cdot \text{s}$ 21. a. rate = $k[\text{NO}]^2[\text{Cl}_2]$; b. 1.8×10^2 L $^2/\text{mol}^2 \cdot \text{min}$ 23. a. rate = $k[\text{NOCl}]^2$; b. 6.6×10^{-29} cm $^3/\text{molecules} \cdot \text{s}$; c. 4.0×10^{-8} L/mol $\cdot$ s 25. a. first order in Hb and first order in CO ; b. rate = $k[\text{Hb}][\text{CO}]$; c. 0.280 L/mol $\cdot$ s; d. 2.26 $\mu\text{mol/L} \cdot \text{s}$ 27. rate = $k[\text{H}_2\text{O}_2]$; $\ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0$; $k = 8.3 \times 10^{-4} \text{ s}^{-1}$; 0.037 M 29. rate = $k[\text{NO}_2]^2$; $\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$; $k = 2.08 \times 10^{-4}$ L/mol $\cdot$ s; 0.131 M 31. a. rate = k ; $[\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0$; since slope = $-k$, then $k = 4.00 \times 10^{-5}$ mol/L $\cdot$ s; b. 156 s; c. 313 s 33. rate = $k[\text{C}_4\text{H}_6]^2$; $\frac{1}{[\text{C}_4\text{H}_6]} = kt + \frac{1}{[\text{C}_4\text{H}_6]_0}$; $k = 1.4 \times 10^{-2}$ L/mol $\cdot$ s 35. second order; 0.1 M 37. a. $[A] = -kt + [A]_0$; b. 1.0×10^{-2} s; c. 2.5×10^{-4} M 39. a. $1.01 \times 10^{-3} \text{ s}^{-1}$; b. 686 s; c. 280 s (25%); 1.4×10^3 s (75%); 3×10^3 s (95%) 41. 0.12 L/mol $\cdot$ s 43. a. 1.1×10^{-3} M; b. 0.025 M 45. a. rate = $k[\text{CH}_3\text{NC}]$; b. rate = $k[\text{O}_3][\text{NO}]$; c. rate = $k[\text{O}_3]$; d. rate = $k[\text{O}_3][\text{O}]$ 47. Rate = $k[\text{C}_4\text{H}_9\text{Br}]$; $\text{C}_4\text{H}_9\text{Br} + 2\text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Br}^- + \text{H}_3\text{O}^+$; the intermediates are C_4H_9^+ and $\text{C}_4\text{H}_9\text{OH}_2^+$.

49.



51. 341 kJ/mol 53. The graph of $\ln k$ versus $1/T$ is linear with slope = $-E_a/R = -1.2 \times 10^4 \text{ K}$; $E_a = 1.0 \times 10^2 \text{ kJ/mol}$ 55. $4.8 \times 10^3 \text{ s}^{-1}$ 57. 51°C 59. $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ should have the faster rate. H_3O^+ and OH^- will be electrostatically attracted to each other; Ce^{4+} and Hg_2^{2+} will repel each other (so E_a is much larger). 61. a. NO; b. NO_2 ; c. 2.3 63. $\text{CH}_2\text{D}-\text{CH}_2\text{D}$ should be the product. If the mechanism is possible, then the reaction must be $\text{C}_2\text{H}_4 + \text{D}_2 \rightarrow \text{CH}_2\text{DCH}_2\text{D}$. If we got this product, then we could conclude that this is a possible mechanism. If we got some other product, e.g., CH_3CHD_2 , then we would conclude that the mechanism is wrong. Even though this mechanism correctly predicts the products of the reaction, we cannot say conclusively that this is the correct mechanism; we might be able to conceive of other mechanisms that would give the same product as our proposed one. 65. 5.68×10^{18} molecules/cm $^3 \cdot \text{s}$ 67. $1.0 \times 10^2 \text{ kJ/mol}$ 69. At high $[\text{S}]$, the enzyme is completely saturated with substrate. Once the enzyme is completely saturated, the rate of decomposition of ES can no longer increase, and the overall rate remains constant. 71. rate = $\frac{k[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$; $k = 6.0 \times 10^1 \text{ s}^{-1}$ 73. a. first order with respect to both reactants; b. rate = $k[\text{NO}][\text{O}_3]$; c. $k' = 1.8 \text{ s}^{-1}$; $k'' = 3.6 \text{ s}^{-1}$; d. $k = 1.8 \times 10^{-14}$ molecules/cm $^3 \cdot \text{s}$ 75. a. 25 kJ/mol; b. 12 s; c.

T	Interval	$54 - 2(\text{Intervals})$
21.0°C	16.3 s	21°C
27.8°C	13.0 s	28°C
30.0°C	12 s	30°C

This rule of thumb gives excellent agreement to two significant figures.

Chapter 13

9. a. The rates of the forward and reverse reactions are equal. b. There is no net change in the composition. 11. The equilibrium position depends on the initial concentrations of an experiment. Since there are an in-

finite number of initial conditions, then there are an infinite number of equilibrium positions. However, each one of these infinite equilibrium positions will always give the same value for the equilibrium constant. **13.** For the gas-phase reaction $aA + bB \rightleftharpoons cC + dD$,

the equilibrium constant expression is $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

and the reaction quotient has the same form $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

The difference is that the expression for K uses equilibrium concentrations; that is, $[A]$, $[B]$, $[C]$, $[D]$ are all in equilibrium with each other. Any set of concentrations can be plugged into the reaction quotient expression. Typically, we plug in initial concentrations into the Q expression, then compare the value of Q to K to see how far we are from equilibrium. If $Q = K$, then the reaction is at equilibrium with these concentrations. If $Q \neq K$, then the reaction will have to shift either to products or to reactants to reach equilibrium. **15.** No, equilibrium is a dynamic process. Both the forward and reverse reactions are occurring at equilibrium, just at equal rates. Thus the forward and reverse reactions will distribute ^{14}C atoms between CO and CO_2 . **17.** 4 molecules H_2O , 2 molecules CO , 4 molecules H_2 , and 4 molecules CO_2 are present at equilibrium

$$19. \text{ a. } K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}, \quad \text{ b. } K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}, \quad \text{ c. } K = \frac{[\text{SiCl}_4][\text{H}_2]^2}{[\text{SiH}_4][\text{Cl}_2]^2},$$

$$\text{d. } K = \frac{[\text{PCl}_3]^2[\text{Br}_2]^3}{[\text{PBr}_3]^2[\text{Cl}_2]^3} \quad 21. \text{ a. } 0.11; \text{ b. } 77; \text{ c. } 8.8; \text{ d. } 1.7 \times 10^{-4}$$

$$23. 6.9 \times 10^{-4} \quad 25. 1.7 \times 10^{-5} \quad 27. 6.3 \times 10^{-13} \quad 29. 1.5 \times 10^8$$

$$31. \text{ a. } K = \frac{1}{[\text{O}_2]^5}, K_p = \frac{1}{P_{\text{O}_2}^5}; \quad \text{ b. } K = [\text{N}_2\text{O}][\text{H}_2\text{O}]^2; K_p = P_{\text{N}_2\text{O}} \times P_{\text{H}_2\text{O}}^2;$$

$$\text{c. } K = \frac{1}{[\text{CO}_2]}, K_p = \frac{1}{P_{\text{CO}_2}}; \quad \text{ d. } K = \frac{[\text{SO}_2]^8}{[\text{O}_2]^8}, K_p = \frac{P_{\text{SO}_2}^8}{P_{\text{O}_2}^8}, \quad 33. 8.0 \times 10^9$$

35. a. $Q > K$, so reaction shifts left to reach equilibrium. b. $Q = K$, so reaction is at equilibrium. c. $Q < K$, so reaction shifts right to reach equilibrium. **37.** a. decrease; b. no change; c. no change; d. increase **39.** 0.096 M **41.** 3.4 **43.** 0.056 **45.** $[\text{SO}_3] = [\text{NO}] = 1.06 \text{ M}$; $[\text{SO}_2] = [\text{NO}_2] = 0.54 \text{ M}$ **47.** $7.8 \times 10^{-2} \text{ atm}$ **49.** $P_{\text{SO}_2} = 0.38 \text{ atm}$; $P_{\text{O}_2} = 0.44 \text{ atm}$; $P_{\text{SO}_3} = 0.12 \text{ atm}$ **51.** a. $[\text{NO}] = 0.032 \text{ M}$, $[\text{Cl}_2] = 0.016 \text{ M}$, $[\text{NOCl}] = 1.0 \text{ M}$; b. $[\text{NO}] = [\text{NOCl}] = 1.0 \text{ M}$, $[\text{Cl}_2] = 1.6 \times 10^{-5} \text{ M}$; c. $[\text{NO}] = 8.0 \times 10^{-3} \text{ M}$, $[\text{Cl}_2] = 1.0 \text{ M}$, $[\text{NOCl}] = 2.0 \text{ M}$ **53.** $[\text{CO}_2] = 0.39 \text{ M}$, $[\text{CO}] = 8.6 \times 10^{-3} \text{ M}$, $[\text{O}_2] = 4.3 \times 10^{-3} \text{ M}$ **55.** 0.27 atm **57.** a. no effect; b. shifts left; c. shifts right **59.** a. right b. right; c. no effect; d. left; e. no effect **61.** a. left; b. right; c. left; d. no effect; e. no effect; f. right **63.** low temperatures **65.** 2.6×10^{81} **67.** $[\text{N}_2]_0 = 10.0 \text{ M}$; $[\text{H}_2]_0 = 11.0 \text{ M}$ **69.** a. 1.16 atm; b. 0.10 atm; c. 2.22 atm; d. 91.4% **71.** $[\text{H}_2] = [\text{F}_2] = 0.0251 \text{ M}$; $[\text{HF}] = 0.450 \text{ M}$ **73.** Added OH^- reacts with H^+ to produce H_2O . As H^+ is removed, the reaction shifts right to produce more H^+ and CrO_4^{2-} . Since more CrO_4^{2-} is produced, then the solution turns yellow. **75.** $[\text{NOCl}] = 2.0 \text{ M}$, $[\text{NO}] = 0.050 \text{ M}$, $[\text{Cl}_2] = 0.025 \text{ M}$ **77.** $2.1 \times 10^{-3} \text{ atm}$ **79.** $P_{\text{NO}_2} = 0.704 \text{ atm}$, $P_{\text{N}_2\text{O}_4} = 0.12 \text{ atm}$ **81.** 0.63

Chapter 14

17. a. Arrhenius acid: produce H^+ in water; b. Brønsted–Lowry acid: proton (H^+) donor; c. Lewis acid: electron-pair acceptor; the Lewis definition is most general. The Lewis definition can apply to all Arrhenius and Brønsted–Lowry acids; H^+ has an empty 1s orbital and forms bonds to all bases by accepting a pair of electrons from the base. In addition, the Lewis definition incorporates other reactions not typically considered acid–base reactions, e.g., $\text{BF}_3(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{F}_3\text{B} \cdot \text{NH}_3(\text{s})$. NH_3 is something we usually consider a base, and it is in this reaction using the Lewis defini-

tion; NH_3 donates a pair of electrons to form the N–B bond. **19.** $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$, pH = 7.00 **21.** An organic compound containing nitrogen with a lone pair of electrons will most likely produce a basic solution. The lone pair of electrons on nitrogen accepts the proton by forming a bond with the proton. **23.** a. stronger bond = stronger base; b. greater electronegativity = weaker base; c. more oxygen atoms = weaker base **25.** a. H_2O and CH_3CO_2^- ; b. CH_3CO_2^- , since the equilibrium favors acetic acid ($K_a < 1$); c. Acetate ion is a better base than water and produces basic solutions in water. When we put acetate ion into solution as the only major basic species, the reaction is



Now the competition is between CH_3CO_2^- and OH^- for the proton. Hydroxide ion is the strongest base possible in water. The above equilibrium favors acetate plus water resulting in a K_b value less than 1. Those species we specifically call weak bases ($10^{-14} < K_b < 1$) lie between H_2O and OH^- in base strength. Weak bases are stronger bases than water but are weaker bases than OH^- . **27.** When an acid dissociates, ions are produced. The conductivity of the solution is a measure of the number of ions. In addition, the colligative properties, as discussed in Chapter 11, depend on the number of particles present. Measurements of osmotic pressure, vapor pressure lowering, freezing-point depression, or boiling-point elevation will also allow us to determine the extent of ionization. **29.** a. $\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ or $\text{HClO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$; water is commonly omitted from K_a reactions. b. $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{CH}_2\text{CO}_2^-(\text{aq})$; c. $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

31.

Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a. HF	H_2O	F^-	H_3O^+
b. H_2SO_4	H_2O	HSO_4^-	H_3O^+
c. HSO_4^-	H_2O	SO_4^{2-}	H_3O^+

33. a. HClO_4 , strong acid; b. HOCl , weak acid; c. H_2SO_4 , strong acid; d. H_2SO_3 , weak acid **35.** $\text{HNO}_3 > \text{HOCl} > \text{NH}_4^+ > \text{H}_2\text{O}$ **37.** a. HCl ; b. HNO_2 ; c. HCN since it has a larger K_a value. **39.** a. $1.0 \times 10^{-7} \text{ M}$; neutral; b. $1.5 \times 10^{-11} \text{ M}$; acidic; c. $5.3 \times 10^{-4} \text{ M}$; basic; d. $4.3 \times 10^{-15} \text{ M}$; acidic **41.** a. endothermic; b. $[\text{H}^+] = [\text{OH}^-] = 2.34 \times 10^{-7} \text{ M}$ **43.** [39] a. pH = pOH = 7.00; b. pH = 3.17; pOH = 10.83; c. pH = 10.72; pOH = 3.28; d. pH = -0.36; pOH = 14.36; [40] a. pH = 14.56; pOH = -0.56; b. pH = 5.99; pOH = 8.01; c. pH = 11.34; pOH = 2.66; d. pH = pOH = 7.00 **45.** pOH = 7.23, $[\text{H}^+] = 1.7 \times 10^{-7} \text{ M}$, $[\text{OH}^-] = 5.9 \times 10^{-8} \text{ M}$, acidic **47.** a. H^+ , ClO_4^- , H_2O ; 0.602; b. H^+ , NO_3^- , H_2O ; 0.602 **49.** $[\text{H}^+] = 0.088 \text{ M}$, $[\text{OH}^-] = 1.1 \times 10^{-13} \text{ M}$, $[\text{Cl}^-] = 0.013 \text{ M}$, $[\text{NO}_3^-] = 0.075 \text{ M}$ **51.** $3.2 \times 10^{-3} \text{ M}$ **53.** a. HNO_2 and H_2O , 2.00; b. $\text{HC}_2\text{H}_3\text{O}_2$ and H_2O , 2.68 **55.** $5.0 \times 10^{-3} \text{ M}$; 2.30 **57.** $[\text{H}^+] = [\text{F}^-] = 3.5 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 2.9 \times 10^{-12} \text{ M}$, $[\text{HF}] = 0.017 \text{ M}$, 2.46 **59.** 1.96 **61.** a. 1.00; b. 1.30 **63.** a. 0.60%; b. 1.9%; c. 5.8%; d. Dilution shifts equilibrium to the side with the greater number of particles (% dissociation increases). e. $[\text{H}^+]$ also depends on initial concentration of weak acid. **65.** 1.4×10^{-4} **67.** 3.5×10^{-4} **69.** 0.024 M **71.** a. $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$



$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

73. $\text{NH}_3 > \text{C}_5\text{H}_5\text{N} > \text{H}_2\text{O} > \text{NO}_3^-$ **75.** a. NH_3 ; b. NH_3 ; c. OH^- ; d. CH_3NH_2 **77.** a. 13.00; b. 7.00; c. 14.30 **79.** a. K^+ , OH^- , and H_2O , 0.015 M, 12.18; b. Ba^{2+} , OH^- , and H_2O , 0.030 M, 12.48 **81.** $3.2 \times 10^{-4} \text{ M}$ **83.** NH_3 and H_2O , $1.6 \times 10^{-3} \text{ M}$, 11.20

85. a. $[\text{OH}^-] = 8.9 \times 10^{-3} \text{ M}$, $[\text{H}^+] = 1.1 \times 10^{-12} \text{ M}$, 11.96; **b.** $[\text{OH}^-] = 4.7 \times 10^{-5} \text{ M}$, $[\text{H}^+] = 2.1 \times 10^{-10} \text{ M}$, 9.68 **87.** 12.00 **89. a.** 1.3%; **b.** 4.2% **91.** 9.2×10^{-7}

93. $\text{H}_2\text{SO}_3(\text{aq}) \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$ K_a , reaction
 $\text{HSO}_3^-(\text{aq}) \rightleftharpoons \text{SO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq})$ K_a , reaction

95. a. 1.62; **b.** 3.68 **97.** -0.30 **99.** $\text{HCl} > \text{NH}_4\text{Cl} > \text{KCl} > \text{KCN} > \text{KOH}$ **101.** OCl^- **103.** $[\text{HN}_3] = [\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}$, $[\text{Na}^+] = 0.010 \text{ M}$, $[\text{N}_3^-] = 0.010 \text{ M}$, $[\text{H}^+] = 4.3 \times 10^{-9} \text{ M}$ **105. a.** 5.82; **b.** 10.95 **107.** NaF **109.** 3.08 **111. a.** neutral; **b.** basic; $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$; **c.** acidic; $\text{C}_5\text{H}_5\text{NH}^+ \rightleftharpoons \text{C}_5\text{H}_5\text{N} + \text{H}^+$; **d.** acidic since NH_4^+ is a stronger acid than NO_2^- is a base; $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$; $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$; **e.** basic; $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$; **f.** basic since OCl^- is a stronger base than NH_4^+ is an acid; $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$, $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ **113. a.** $\text{HIO}_3 < \text{HBrO}_3$; as the electronegativity of the central atom increases, acid strength increases. **b.** $\text{HNO}_2 < \text{HNO}_3$; as the number of oxygen atoms attached to the central atom increases, acid strength increases. **c.** $\text{HOI} < \text{HOCl}$; same reasoning as in part a. **d.** $\text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_4$; same reasoning as in part b. **115. a.** $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$; acid strength increases as bond energy decreases. **b.** $\text{CH}_3\text{CO}_2\text{H} < \text{FCH}_2\text{CO}_2\text{H} < \text{F}_2\text{CHCO}_2\text{H} < \text{F}_3\text{CCO}_2\text{H}$; as the electronegativity of the neighboring atoms increases, acid strength increases. **c.** $\text{NH}_4^+ < \text{HONH}_3^+$; same reasoning as in part b. **d.** $\text{NH}_4^+ < \text{PH}_4^+$; same reasoning as in part a. **117. a.** basic; $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$; **b.** acidic; $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$; **c.** acidic; $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HOCl}(\text{aq})$ **119. a.** $\text{B}(\text{OH})_3$, acid; H_2O , base; **b.** Ag^+ , acid; NH_3 , base; **c.** BF_3 , acid; F^- , base **121.** $\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq})$ **123.** Fe^{3+} ; because it is smaller with a greater positive charge, Fe^{3+} will be more strongly attracted to a lone pair of electrons from a Lewis base. **125.** 990 mL H_2O **127.** NH_4Cl **129.** 3.00 **131. a.** 2.62; **b.** 2.4%; **c.** 8.48 **133. a.** 1.66; **b.** Fe^{2+} ions will produce a less acidic solution (higher pH) due to the lower charge on Fe^{2+} as compared with Fe^{3+} . As the charge on a metal ion increases, acid strength of the hydrated ion increases. **135.** acidic; $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$; 1.54 **137. a.** $\text{Hb}(\text{O}_2)_4$ in lungs, HbH_4^{4+} in cells; **b.** Decreasing $[\text{CO}_2]$ will decrease $[\text{H}^+]$, favoring $\text{Hb}(\text{O}_2)_4$ formation. Breathing into a bag raises $[\text{CO}_2]$. **c.** NaHCO_3 lowers the acidity from accumulated CO_2 . **139. a.** H_2SO_3 ; **b.** HClO_3 ; **c.** H_3PO_3 ; NaOH and KOH are ionic compounds composed of either Na^+ or K^+ cations and OH^- anions. When soluble ionic compounds dissolve in water, they form the ions from which they are formed. The acids in this problem are all covalent compounds. When these acids dissolve in water, the covalent bond between oxygen and hydrogen breaks to form H^+ ions. **141.** 7.20. **143.** 7.4; when an acid is added to water, the pH cannot be basic. Must account for the autoionization of water. **145.** 0.022 M **147.** PO_4^{3-} , $K_b = 0.021$; HPO_4^{2-} , $K_b = 1.6 \times 10^{-7}$; H_2PO_4^- , $K_b = 1.3 \times 10^{-12}$; from the K_b values, PO_4^{3-} is the strongest base. **149.** 1.0×10^{-3}

Chapter 15

13. A common ion is an ion that appears in an equilibrium reaction but came from a source other than that reaction. Addition of a common ion (H^+ or NO_2^-) to the reaction $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ will drive the equilibrium to the left as predicted by Le Châtelier's principle. **15.** No, as long as there are both a weak acid and a weak base present, the solution will be buffered. If the concentrations are the same, the buffer will have the same capacity toward both added H^+ and OH^- . **17.** No, since there are three colored forms, there must be two proton transfer reactions. Thus there must be at least two acidic protons in the acid (orange) form of thymol blue. **19.** The two forms of an indicator are different colors. To see only one color, that form must be in tenfold excess or greater over the other. When the ratio of the two forms is less than 10, both colors are present. To go from $[\text{HIn}]/[\text{In}^-] = 10$ to $[\text{HIn}]/[\text{In}^-] = 0.1$ requires a change of 2 pH units as the indicator changes from the acid color to the base color. **21.** When strong acid or strong base is added to a sodium bicarbonate/sodium carbonate buffer mixture, the strong acid/base is neutralized. The reaction goes to completion resulting in the strong acid/base

being replaced with a weak acid/base. This results in a new buffer solution. The reactions are $\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$; $\text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ **23. a.** 2.96; **b.** 8.94; **c.** 7.00; **d.** 4.89 **25.** 1.1% vs. $1.3 \times 10^{-2}\%$ dissociated; the presence of $\text{C}_3\text{H}_5\text{O}_2^-$ in solution 23d greatly inhibits the dissociation of $\text{HC}_3\text{H}_5\text{O}_2$. This is called the *common ion effect*. **27. a.** 1.70; **b.** 5.49; **c.** 1.70; **d.** 4.71 **29. a.** 4.29; **b.** 12.30; **c.** 12.30; **d.** 5.07 **31.** solution d; solution d is a buffer solution that resists pH changes. **33.** 3.40 **35.** 3.48; 3.22 **37. a.** 5.14; **b.** 4.34; **c.** 4.74; **d.** 11.04; **e.** 10.74 **39. a.** 7.97; **b.** 8.73; both solutions have an initial pH = 8.77. The two solutions differ in their buffer capacity. Solution b with the larger concentrations has the greater capacity to resist pH change. **41.** 15 g **43. a.** 0.19; **b.** 0.59; **c.** 1.0; **d.** 1.9 **45.** HOCl ; there are many possibilities. One possibility is a solution with $[\text{HOCl}] = 1.0 \text{ M}$ and $[\text{NaOCl}] = 0.35 \text{ M}$. **47.** solution d **49. a.** 1.0 mol; **b.** 0.30 mol; **c.** 1.3 mol **51. a.** ~22 mL base added; **b.** buffer region is from ~1 mL to ~21 mL base added. The maximum buffering region would be from ~5 mL to ~17 mL of base added with the halfway point to equivalence (~11 mL) as the best buffer point. **c.** ~11 mL base added; **d.** 0 mL base added; **e.** ~22 mL base added (the stoichiometric point); **f.** any point after the stoichiometric point (volume base added > ~22 mL) **53. a.** 0.699; **b.** 0.854; **c.** 1.301; **d.** 7.00; **e.** 12.15 **55. a.** 2.72; **b.** 4.26; **c.** 4.74; **d.** 5.22; **e.** 8.79; **f.** 12.15

57. Volume (mL)	pH
0.0	2.43
4.0	3.14
8.0	3.53
12.5	3.86
20.0	4.46
24.0	5.24
24.5	5.6
24.9	6.3
25.0	8.28
25.1	10.3
26.0	11.29
28.0	11.75
30.0	11.96

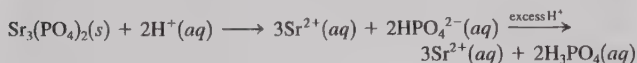
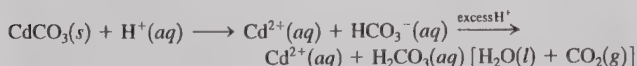
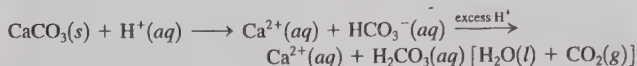
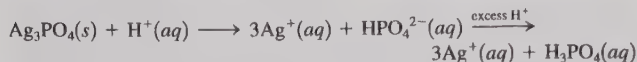
See *Solutions Guide* for pH plot.

59. Volume (mL)	pH
0.0	11.11
4.0	9.97
8.0	9.58
12.5	9.25
20.0	8.65
24.0	7.87
24.5	7.6
24.9	6.9
25.0	5.28
25.1	3.7
26.0	2.71
28.0	2.24
30.0	2.04

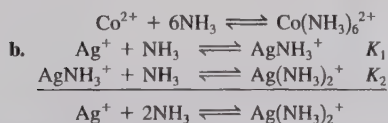
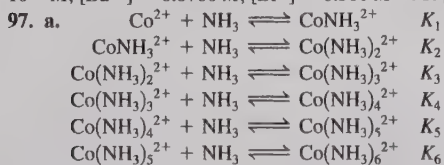
See *Solutions Guide* for pH plot.

61. a. 4.19, 8.45; **b.** 10.74; 5.96; **c.** 0.89, 7.00 **63.** 1.74×10^{-8} **65. a.** yellow; **b.** 8.0; **c.** blue **67.** Phenol red is one possible indicator for the titration in Exercise 53. Phenolphthalein is one possible indicator for the titration in Exercise 55. **69.** Phenolphthalein is one possible indicator for Exercise 57. Bromocresol green is one possible indicator for Exercise 59. **71.** The pH is between 5 and 8. **73. a.** $\text{AgC}_2\text{H}_3\text{O}_2(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$; $K_{sp} = [\text{Ag}^+][\text{C}_2\text{H}_3\text{O}_2^-]$; **b.** $\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq})$; $K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3$; **c.** $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$; $K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$ **75. a.** 2.3×10^{-9} ; **b.** 8.20×10^{-19} **77.** 3.92×10^{-5} **79. a.** $1.6 \times 10^{-5} \text{ mol/L}$; **b.** $9.3 \times$

10^{-5} mol/L; **c.** 6.5×10^{-7} mol/L **81.** 2.5×10^{-22} mol/L **83. a.** CaF_2 ; **b.** FePO_4 **85. a.** 4×10^{-17} mol/L; **b.** 4×10^{-11} mol/L; **c.** 4×10^{-29} mol/L **87.** 2.3×10^{-11} mol/L **89.** If the anion in the salt can act as a base in water, then the solubility of the salt will increase as the solution becomes more acidic. Added H^+ will react with the base, forming the conjugate acid. As the basic anion is removed, more of the salt will dissolve to replenish the basic anion. The salts with basic anions are Ag_3PO_4 , CaCO_3 , CdCO_3 , and $\text{Sr}_3(\text{PO}_4)_2$. Hg_2Cl_2 and PbI_2 do not have any pH dependence because Cl^- and I^- are terrible bases (the conjugate bases of strong acids).



91. yes; $Q = 1.9 \times 10^{-4} > K_{\text{sp}}$ **93.** $[\text{K}^+] = 0.160 \text{ M}$, $[\text{C}_2\text{O}_4^{2-}] = 3.3 \times 10^{-7} \text{ M}$, $[\text{Ba}^{2+}] = 0.0700 \text{ M}$, $[\text{Br}^-] = 0.300 \text{ M}$ **95.** $[\text{Ag}^+] > 5.6 \times 10^{-5} \text{ M}$



99. $\text{Hg}_2^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{HgI}_2(\text{s})$ (orange precipitate); $\text{HgI}_2(\text{s}) + 2\text{I}^-(\text{aq}) \rightarrow \text{HgI}_4^{2-}(\text{aq})$ (soluble complex ion) **101.** $3.3 \times 10^{-32} \text{ M}$ **103. a.** $1.2 \times 10^{-8} \text{ mol/L}$; **b.** $1.5 \times 10^{-4} \text{ mol/L}$; **c.** The presence of NH_3 increases the solubility of AgI . Added NH_3 removes Ag^+ from solution by forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$. As Ag^+ is removed, more AgI will dissolve to replenish the Ag^+ concentration. **105.** Test tube 1: added Cl^- reacts with Ag^+ to form the silver chloride precipitate. The net ionic equation is $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$. Test tube 2: added NH_3 reacts with Ag^+ ions to form the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$. As this complex ion forms, Ag^+ is removed from solution, which causes $\text{AgCl}(\text{s})$ to dissolve. When enough NH_3 is added, then all of the silver chloride precipitate will dissolve. The equation is $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$. Test tube 3: added H^+ reacts with the weak base NH_3 to form NH_4^+ . As NH_3 is removed, Ag^+ ions are released to solution, which can then react with Cl^- to reform $\text{AgCl}(\text{s})$. The equations are $\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ag}^+(\text{aq}) + 2\text{NH}_4^+(\text{aq})$ and $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$.

107. $\text{pOH} = \text{p}K_{\text{b}} + \log \frac{[\text{acid}]}{[\text{base}]}$ **109. a.** potassium fluoride + HCl ;

b. benzoic acid + NaOH ; **c.** acetic acid + sodium acetate; **d.** HOCl + NaOH ; **e.** ammonium chloride + NaOH **111. a.** 1.8×10^6 ; **b.** 5.6×10^4 ; **c.** 1.0×10^{14} **113.** 4.4 L **115.** $180. \text{ g/mol}$; 3.3×10^{-4} ; assume acetylsalicylic acid is a weak monoprotic acid. **117.** 0.210 M **119.** $2.7 \times 10^{-5} \text{ mol/L}$; the solubility of hydroxyapatite will increase as a solution gets more acidic, since both phosphate and hydroxide can react with H^+ . $6 \times 10^{-8} \text{ mol/L}$; the hydroxyapatite in the tooth enamel is converted to the less soluble fluorapatite by fluoride-treated water. The less soluble fluorapatite will then be more difficult to dissolve, making teeth less susceptible to decay. See Chemical Impact on "Chemistry of Teeth." **121. a.** $6.7 \times 10^{-6} \text{ mol/L}$; **b.** $1.2 \times 10^{-13} \text{ mol/L}$; **c.** $\text{Pb}(\text{OH})_2(\text{s})$ will not

form since $Q < K_{\text{sp}}$ **123.** 49 mL **125.** 3.9 L **127. a.** 200.0 mL ; **b.** i. H_2A , H_2O ; ii. H_2A , HA^- , H_2O , Na^+ ; iii. HA^- , H_2O , Na^+ ; iv. HA^- , A^{2-} , H_2O , Na^+ ; v. A^{2-} , H_2O , Na^+ ; vi. A^{2-} , H_2O , Na^+ , OH^- ; **c.** $K_{\text{a}} = 1 \times 10^{-4}$; $K_{\text{a}} = 1 \times 10^{-8}$ **129. a.** $5.8 \times 10^{-4} \text{ mol/L}$; **b.** Greater; F^- is a weak base ($K_{\text{b}} = 1.4 \times 10^{-11}$), so some of the F^- is removed by reaction with water. As F^- is removed, more SrF_2 will dissolve; **c.** $3.5 \times 10^{-3} \text{ mol/L}$

Chapter 16

7. a. A spontaneous process occurs without any outside intervention. **b.** Entropy is a measure of disorder or randomness. **c.** The system is the portion of the universe in which we are interested. **d.** The surroundings are everything else in the universe besides the system. **9.** Living organisms need an external energy source to produce the necessary "ordering." **11.** The more widely something is dispersed, the greater the disorder and the greater the work needed to overcome the disorder. It would be more advantageous to prevent contamination of the environment rather than clean it up later. **13.** $w_{\text{max}} = \Delta G$; when ΔG is negative, the magnitude of ΔG is equal to the maximum possible useful work obtainable from the process (at constant T and P). When ΔG is positive, the magnitude of ΔG is equal to the minimum amount of work that must be expended to make the process spontaneous. Due to waste energy (heat) in any real process, the amount of useful work obtainable from a spontaneous process is always less than w_{max} , and for a nonspontaneous reaction, an amount of work greater than w_{max} must be applied to make the process spontaneous. **15. a, b, c** **17.** We draw all of the possible arrangements of the two particles in the three levels.

2 kJ	—	—	<u>X</u>	—	<u>X</u>	<u>XX</u>
1 kJ	—	<u>X</u>	—	<u>XX</u>	<u>X</u>	—
0 kJ	<u>XX</u>	<u>X</u>	<u>X</u>	—	—	—
Total $E =$	0 kJ	1 kJ	2 kJ	2 kJ	3 kJ	4 kJ

The most likely total energy is 2 kJ. **19. a.** H_2 at 100°C and 0.5 atm ; **b.** N_2 at STP; **c.** $\text{H}_2\text{O}(\text{l})$ **21. a.** negative; **b.** positive **23.** $\Delta G < 0$ for **b, c, d** **25.** $89.3 \text{ J/K} \cdot \text{mol}$ **27. a.** yes ($\Delta G < 0$); **b.** 196 K **29. a.** negative; **b.** positive; **c.** negative; **d.** positive **31. a.** $\text{C}_{\text{graphite}}(\text{s})$; **b.** $\text{C}_2\text{H}_5\text{OH}(\text{g})$; **c.** $\text{CO}_2(\text{g})$ **33. a.** negative, -186 J/K ; **b.** positive, 187 J/K ; **c.** hard to predict since $\Delta n = 0$; 138 J/K **35.** $262 \text{ J/K} \cdot \text{mol}$ **37. a.** ΔH and ΔS are both positive; **b.** S_{rhombic} **39. a.** ΔH and ΔS are both negative; **b.** low temperatures **41. a.** $\Delta H^\circ = -803 \text{ kJ}$, $\Delta S^\circ = -4 \text{ J/K}$, $\Delta G^\circ = -802 \text{ kJ}$; **b.** $\Delta H^\circ = 2802 \text{ kJ}$, $\Delta S^\circ = -262 \text{ J/K}$, $\Delta G^\circ = 2880. \text{ kJ}$; **c.** $\Delta H^\circ = -416 \text{ kJ}$, $\Delta S^\circ = -209 \text{ J/K}$, $\Delta G^\circ = -354 \text{ kJ}$; **d.** $\Delta H^\circ = -176 \text{ kJ}$, $\Delta S^\circ = -284 \text{ J/K}$, $\Delta G^\circ = -91 \text{ kJ}$ **43.** $\text{CH}_4(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CH}_3\text{CO}_2\text{H}(\text{l})$, $\Delta H^\circ = -16 \text{ kJ}$, $\Delta S^\circ = -240. \text{ J/K}$, $\Delta G^\circ = 56 \text{ kJ}$; $\text{CH}_3\text{OH}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CH}_3\text{CO}_2\text{H}(\text{l})$, $\Delta H^\circ = -173 \text{ kJ}$, $\Delta S^\circ = -278 \text{ J/K}$, $\Delta G^\circ = -90. \text{ kJ}$; the second reaction is preferred. It should be run at temperatures below 622 K . **45.** $-300. \text{ kJ}$ **47.** -731 kJ/mol **49.** -4172 kJ **51.** -188 kJ **53. a.** shifts right; **b.** no shift since the reaction is at equilibrium; **c.** shifts left **55.** 8.72 ; 0.0789 **57. a.** 79.9 kJ/mol ; **b.** 81.1 kJ/mol **59.** -71 kJ/mol **61.** $\Delta H^\circ = 1.1 \times 10^5 \text{ J/mol}$; $\Delta S^\circ = 330 \text{ J/K} \cdot \text{mol}$; The major difference in the plot is the slope of the line. An endothermic process has a negative slope for the $\ln(K)$ versus $1/T$ plot, whereas an exothermic process has a positive slope. **63.** ΔS_{univ} **65.** The introduction of mistakes is an effect of entropy. The purpose of redundant information is to provide a control to check the "correctness" of the transmitted information. **67.** 370 K **69.** 60 **71. a.** $1.8 \times 10^4 \text{ J/mol}$; shifts left; **b.** 0 ; no shift since at equilibrium; **c.** $-1.1 \times 10^4 \text{ J/mol}$; shifts right; **d.** 0 ; no shift since at equilibrium; **e.** $2 \times 10^3 \text{ J/mol}$; shifts left **73. a.** 2.22×10^5 ; **b.** 94.3 **75.** ΔS is more favorable for reaction 2 than for reaction 1, resulting in $K_2 > K_1$. In reaction 1, seven particles in solution form one particle. In reaction 2, four particles form one, which

results in a smaller decrease in disorder than for reaction 1. **77.** $\Delta H^\circ = 286 \text{ kJ}$; $\Delta G^\circ = 326 \text{ kJ}$; $K = 7.22 \times 10^{-58}$; $P_{\text{O}_3} = 3.3 \times 10^{-41} \text{ atm}$; This partial pressure represents one molecule of ozone per $9.5 \times 10^{17} \text{ L}$ of air. Equilibrium is probably not maintained under the conditions because the concentration of ozone is not large enough to maintain equilibrium

79. a. Since $k_f = A \exp\left(\frac{-E_a}{RT}\right)$ and $k_r = A \exp\left(\frac{-(E_a - \Delta G^\circ)}{RT}\right)$, then $\frac{k_f}{k_r} = \exp\left(\frac{-E_a}{RT} + \frac{(E_a - \Delta G^\circ)}{RT}\right) = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$. Since $K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$, then $K = \frac{k_f}{k_r}$. **b.** A catalyst increases the value of the rate constant (increases rate) by lowering the activation energy. For the equilibrium constant K to remain constant, both k_f and k_r must increase by the same factor. Therefore, a catalyst must increase the rate of both the forward and the reverse reactions. **81. a.** 0.333; **b.** $P_A = 1.50 \text{ atm}$; $P_B = 0.50 \text{ atm}$; **c.** $\Delta G = \Delta G^\circ + RT \ln(P_B/P_A) = 2722 \text{ J} - 2722 \text{ J} = 0$ **83.** at least 7.5 torr **85.** 16 g

Chapter 17

13. Oxidation: increase in oxidation number, loss of electrons; reduction: decrease in oxidation number, gain of electrons **15.** Reactions a, b, and c are oxidation–reduction reactions.

Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. H_2O	CH_4	$\text{CH}_4(\text{C})$	$\text{H}_2\text{O}(\text{H})$
b. AgNO_3	Cu	Cu	$\text{AgNO}_3(\text{Ag})$
c. HCl	Zn	Zn	$\text{HCl}(\text{H})$

17. In a galvanic cell a spontaneous reaction occurs, producing an electric current. In an electrolytic cell electricity is used to force a reaction to occur that is not spontaneous. **19. a.** cathode: where reduction occurs; **b.** anode: where oxidation occurs; **c.** oxidation half-reaction: e^- are products; **d.** reduction half-reaction: e^- are reactants **21.** As a battery discharges, $\mathcal{E}_{\text{cell}}$ decreases, eventually reaching zero. A charged battery is not at equilibrium. At equilibrium, $\mathcal{E}_{\text{cell}} = 0$ and $\Delta G = 0$. We get no work out of an equilibrium system. A battery is useful to us because it can do work as it approaches equilibrium. **23.** Both fuel cells and batteries are galvanic cells. However, fuel cells, unlike batteries, have the reactants continuously supplied and can produce a current indefinitely. **25.** See Figure 17.2 of the text for a typical galvanic cell. The anode compartment contains the oxidation half-reaction compounds/ions, and the cathode compartment contains the reduction half-reaction compounds/ions. The electrons flow from the anode to the cathode. For each of the following answers, all solutes are 1.0 M and all gases are at 1.0 atm. **a.** $7\text{H}_2\text{O}(\text{l}) + 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cl}_2(\text{g}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Cl}^-(\text{aq}) + 14\text{H}^+(\text{aq})$; cathode: Pt electrode; Cl_2 bubbled into solution, Cl^- in solution; anode: Pt electrode; Cr^{3+} , H^+ , and $\text{Cr}_2\text{O}_7^{2-}$ in solution; **b.** $\text{Cu}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Mg}^{2+}(\text{aq})$; cathode: Cu electrode; Cu^{2+} in solution; anode: Mg electrode; Mg^{2+} in solution **27. a.** 0.03 V; **b.** 2.71 V **29.** See Exercise 25 for a description of a galvanic cell. For each of the following answers, all solutes are 1.0 M and all gases are at 1.0 atm. In the salt bridge, cations flow to the cathode and anions flow to the anode. **a.** $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$ $\mathcal{E}^\circ = 0.27 \text{ V}$; cathode: Pt electrode; $\text{Cl}_2(\text{g})$ bubbled in, Cl^- in solution; anode: Pt electrode; Br_2 and Br^- in solution; **b.** $3\text{H}_2\text{O}(\text{l}) + 5\text{IO}_4^-(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) \rightarrow 5\text{IO}_3^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq})$ $\mathcal{E}^\circ = 0.09 \text{ V}$; cathode: Pt electrode; IO_4^- , IO_3^- , and H_2SO_4 (as a source of H^+) in solution; anode: Pt electrode; Mn^{2+} , MnO_4^- , and H_2SO_4 in solution **31.** 25a. $\text{Pt}|\text{Cr}^{3+}(1.0 \text{ M}), \text{H}^+(1.0 \text{ M}), \text{Cr}_2\text{O}_7^{2-}(1.0 \text{ M})||\text{Cl}_2(1.0 \text{ atm})|\text{Cl}^-(1.0 \text{ M})| \text{Pt}$; 25b. $\text{Mg}|\text{Mg}^{2+}(1.0 \text{ M})||\text{Cu}^{2+}(1.0 \text{ M})|\text{Cu}$; 29a. $\text{Pt}|\text{Br}^-(1.0 \text{ M}), \text{Br}_2(1.0 \text{ M})||\text{Cl}_2(1.0 \text{ atm})|\text{Cl}^-(1.0 \text{ M})| \text{Pt}$; 29b.

$\text{Pt}|\text{Mn}^{2+}(1.0 \text{ M}), \text{MnO}_4^-(1.0 \text{ M}), \text{H}^+(1.0 \text{ M})||\text{IO}_4^-(1.0 \text{ M}), \text{H}^+(1.0 \text{ M})|\text{IO}_3^-(1.0 \text{ M})| \text{Pt}$ **33. a.** $\text{Au}^{3+}(\text{aq}) + 3\text{Cu}^+(\text{aq}) \rightarrow 3\text{Cu}^{2+}(\text{aq}) + \text{Au}(\text{s})$ $\mathcal{E}^\circ = 1.34 \text{ V}$; **b.** $2\text{VO}_2^+(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{VO}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ = 1.40 \text{ V}$ **35. a.** $\mathcal{E}^\circ = 0.46 \text{ V}$, spontaneous; **b.** $\mathcal{E}^\circ = -0.53 \text{ V}$, not spontaneous **37. \mathcal{E}^\circ = 0.41 \text{ V}, $\Delta G^\circ = -79 \text{ kJ}$ **39. 33a.** -388 kJ ; **33b.** $-270. \text{ kJ}$ **41.** 1.21 V **43.** $\text{K}^+ < \text{H}_2\text{O} < \text{Cd}^{2+} < \text{I}_2 < \text{AuCl}_4^- < \text{IO}_3^-$ **45. a.** no; **b.** yes; **c.** yes; **d.** no **47. a.** $\text{Cr}_2\text{O}_7^{2-}$, O_2 , MnO_2 , IO_3^- ; **b.** PbSO_4 , Cd^{2+} , Fe^{2+} , Cr^{3+} , Zn^{2+} , H_2O **49.** $\text{ClO}^-(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ_{\text{cell}} = 1.00 \text{ V}$; Since $\mathcal{E}^\circ_{\text{cell}}$ is positive for this reaction, then at standard conditions ClO^- can spontaneously oxidize NH_3 to the somewhat toxic N_2H_4 . **51. a.** larger; **b.** smaller **53.** Electron flow is always from the anode to the cathode. For the cells with a nonzero cell potential, we will identify the cathode, which means the other compartment is the anode. **a.** 0; **b.** 0.018 V; compartment with $[\text{Ag}^+] = 2.0 \text{ M}$ is cathode; **c.** 0.059 V; compartment with $[\text{Ag}^+] = 1.0 \text{ M}$ is cathode; **d.** 0.26 V; compartment with $[\text{Ag}^+] = 1.0 \text{ M}$ is cathode; **e.** 0 **55. yes** **57.** 1.09 V **59. a.** 0.23 V; **b.** $1.2 \times 10^{-5} \text{ M}$ **61.** 0.16 V, copper is oxidized. **63. [25] a.** $\Delta G^\circ = -20 \text{ kJ}$; 1×10^3 ; **b.** $\Delta G^\circ = -523 \text{ kJ}$; 5.12×10^{91} ; **[29] a.** $\Delta G^\circ = -52 \text{ kJ}$; 1.4×10^9 ; **b.** $\Delta G^\circ = -90 \text{ kJ}$; 2×10^{15} **65. a.** no reaction; **b.** $\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2\text{Cl}^-(\text{aq})$ $\mathcal{E}^\circ_{\text{cell}} = 0.82 \text{ V}$, $\Delta G^\circ = -160 \text{ kJ}$; $K = 5.6 \times 10^{27}$; **c.** no reaction; **d.** $4\text{Fe}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ_{\text{cell}} = 0.46 \text{ V}$, $\Delta G^\circ = -180 \text{ kJ}$; $K = 1.3 \times 10^{31}$; **67. a.** $\text{Au}^{3+}(\text{aq}) + 3\text{Ti}(\text{s}) \rightarrow \text{Au}(\text{s}) + 3\text{Ti}^+(\text{aq})$ $\mathcal{E}^\circ_{\text{cell}} = 1.84 \text{ V}$; **b.** $\Delta G^\circ = -533 \text{ kJ}$; $K = 2.52 \times 10^{93}$; **c.** 2.04 V **69.** 3.9×10^{-28} **71.** 1.6×10^{13} **73. a.** 30. hours; **b.** 33 s; **c.** 1.3 hours **75. a.** 16 g; **b.** 25 g; **c.** 71 g; **d.** 4.9 g **77. Sc** **79.** 9.12 L F_2 (anode), 29.2 g K (cathode) **81.** $7.44 \times 10^4 \text{ A}$ **83.** $1.14 \times 10^{-2} \text{ M}$ **85.** Au followed by Ag followed by Ni followed by Cd **87. a.** cathode: $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$; anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$; **b.** cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$; anode: $2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$; **c.** cathode: $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$; anode: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ **89. a.** 0.10 V, SCE is anode; **b.** 0.53 V, SCE is anode; **c.** 0.02 V, SCE is cathode; **d.** 1.90 V, SCE is cathode; **e.** 0.47 V, SCE is cathode **91. a.** decrease; **b.** increase; **c.** decrease; **d.** decrease; **e.** same **93. a.** $\Delta G^\circ = -582 \text{ kJ}$; $K = 3.45 \times 10^{102}$; $\mathcal{E}^\circ = 1.01 \text{ V}$; **b.** -0.65 V ; **95.** The concentrations were such that $\text{Cr}_2\text{O}_7^{2-}$ oxidized Cl^- to form pungent fumes of $\text{Cl}_2(\text{g})$. **97.** The claim is impossible. The strongest oxidizing agent and reducing agent when combined only give $\mathcal{E}^\circ$ of about 6 V. **99.** $w_{\text{max}} = -13,200 \text{ kJ}$; the work done can be no larger than the free energy change. If the process were reversible all of the free energy released would go into work, but this does not occur in any real process. Fuel cells are more efficient in converting chemical energy to electrical energy; they are also less massive. Major disadvantage: They are expensive. **101.** 0.98 V **103.** +3 **105.** $\mathcal{E}^\circ = \frac{T\Delta S^\circ}{nF} - \frac{\Delta H^\circ}{nF}$; if**

we graph $\mathcal{E}^\circ$ vs. T , we should get a straight line ($y = mx + b$). The slope of the line is equal to $\Delta S^\circ/nF$ and the y-intercept is equal to $-\Delta H^\circ/nF$. $\mathcal{E}^\circ$ will have little temperature dependence for cell reactions with ΔS° close to zero. **107.** 9.8×10^{-6} **109.** 2.39×10^{-7} **111. a.** ± 0.02 pH units; $\pm 6 \times 10^{-6} \text{ M H}^+$; **b.** $\pm 0.001 \text{ V}$ **113. a.** 0.16 V; **b.** 8.6 mol

Chapter 18

1. Fission: Splitting of a heavy nucleus into two (or more) lighter nuclei.

Fusion: Combining two light nuclei to form a heavier nucleus.

The maximum binding energy per nucleon occurs at Fe. Nuclei smaller than Fe become more stable by fusing to form heavier nuclei closer to Fe. Nuclei larger than Fe form more stable nuclei by splitting to form lighter nuclei closer to Fe. **3.** Assume ^{14}C level is constant or can be determined at the time the object died. Constant ^{14}C level is a poor assumption and accounting for variation is complicated. Also, some of the material must be destroyed. **5.** No, coal-fired power plants also pose risks. A partial list of risks:

Coal	Nuclear
Air pollution	Radiation exposure to workers
Coal mine accidents	Disposal of wastes
Health risks to miners	Meltdown
(black lung disease)	Terrorists
	Public fear

7. For fusion a collision of sufficient energy must occur between two positively charged particles to initiate the reaction. This requires high temperatures. In fission, an electrically neutral neutron collides with the positively charged nucleus. This has a much lower activation energy. 9. a. ${}^{51}_{24}\text{Cr} + {}^0_{-1}\text{e} \rightarrow {}^{51}_{23}\text{V}$; b. ${}^{131}_{53}\text{I} \rightarrow {}^0_{-1}\text{e} + {}^{131}_{54}\text{Xe}$ 11. a. ${}^{68}_{31}\text{Ga} + {}^0_{-1}\text{e} \rightarrow {}^{68}_{30}\text{Zn}$; b. ${}^{62}_{29}\text{Cu} \rightarrow {}^0_{+1}\text{e} + {}^{62}_{28}\text{Ni}$; c. ${}^{212}_{87}\text{Fr} \rightarrow {}^4_2\text{He} + {}^{208}_{85}\text{At}$; d. ${}^{129}_{51}\text{Sb} \rightarrow {}^0_{-1}\text{e} + {}^{129}_{52}\text{Te}$ 13. 10 α particles; 5 β particles 15. ${}^{53}_{26}\text{Fe}$ has too many protons. It will undergo positron production, electron capture, and/or alpha-particle production. ${}^{59}_{26}\text{Fe}$ has too many neutrons and will undergo beta-particle production. (See Table 18.2 of the text.) 17. a. ${}^{249}_{98}\text{Cf} + {}^{18}_8\text{O} \rightarrow {}^{263}_{106}\text{Sg} + {}^4_{10}\text{n}$; b. ${}^{259}_{104}\text{Rf}$ 19. 690 hours 21. ${}^{81}_{36}\text{Kr}$ is most stable since it has the longest half-life. ${}^{73}_{36}\text{Kr}$ is "hottest" since it decays very rapidly due to its very short half-life. ${}^{73}_{36}\text{Kr}$, 81s; ${}^{74}_{36}\text{Kr}$, 34.5 min; ${}^{76}_{36}\text{Kr}$, 44.4 h; ${}^{81}_{36}\text{Kr}$, 6.3×10^5 yr 23. 6.22 mg ${}^{32}_{15}\text{P}$ remains 25. 0.247 27. 2.3 counts per minute per gram of C. No; for a 10.-mg C sample, it would take roughly 40 min to see a single disintegration. This is too long to wait, and the background radiation would probably be much greater than the ${}^{14}\text{C}$ activity. Thus ${}^{14}\text{C}$ dating is not practical for very small samples. 29. 3.8×10^9 yr 31. 4.3×10^6 kg/s 33. ${}^{232}_{90}\text{Pu}$, -1.715×10^{14} J/mol; ${}^{231}_{91}\text{Pa}$, -1.714×10^{14} J/mol 35. ${}^{12}\text{C}$: 1.23×10^{-12} J/nucleon; ${}^{235}\text{U}$: 1.2155×10^{-12} J/nucleon; since ${}^{56}\text{Fe}$ is the most stable known nucleus, then the binding energy per nucleon for ${}^{56}\text{Fe}$ would be larger than that of ${}^{12}\text{C}$ or ${}^{235}\text{U}$. (See Fig. 18.9 of the text.) 37. -2.0×10^{10} J/g of hydrogen nuclei 39. The Geiger-Müller tube has a certain response time. After the gas in the tube ionizes to produce a "count," some time must elapse for the gas to return to an electrically neutral state. The response of the tube levels off because at high activities radioactive particles are entering the tube faster than the tube can respond to them. 41. All evolved $\text{O}_2(\text{g})$ comes from water. 43. Strontium. Xe is chemically unreactive and not readily incorporated into the body. Sr can be easily oxidized to Sr^{2+} . Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca^{2+} . The chemical properties determine where radioactive material may be concentrated in the body or how easily it may be excreted. 45. a. unstable; beta production; b. stable; c. unstable; positron production or electron capture; d. unstable, positron production, electron capture, or alpha production. 47. 1975 49. 900 g ${}^{235}\text{U}$ 51. Assuming that (1) the radionuclide is long lived enough that no significant decay occurs during the time of the experiment, and (2) the total activity is uniformly distributed only in the rat's blood; $V = 10$ mL. 53. a. ${}^{12}_6\text{C}$; b. ${}^{13}_6\text{C}$, ${}^{13}_7\text{N}$, ${}^{15}_7\text{N}$, and ${}^{15}_8\text{O}$; c. -5.950×10^{11} J/mol ${}^1\text{H}$ 55. 4.3×10^{-29}

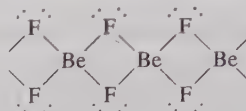
Chapter 19

1. The gravity of the earth cannot keep H_2 in the atmosphere. 3. Ionic, covalent, and metallic (or interstitial). The ionic and covalent hydrides are true compounds that differ in the type of bonding. The interstitial hydrides are more like solid solutions of hydrogen and a transition metal and have variable content. 5. Hydrogen forms many compounds in which its oxidation state is +1. On the other hand, hydrogen forms diatomic H_2 molecules and is a nonmetal, while the Group 1A elements are metals. Hydrogen forms the hydride anion H^- ; the Group 1A metals do not form stable anions. 7. They must be produced in the absence of materials (H_2O , O_2) that are capable of oxidizing them. 9. The planes of carbon atoms slide easily. Graphite is not volatile so the lubricant will not be lost when used in a high vacuum environment. 11. p-type semiconductor 13. a. $\Delta H^\circ = 207$ kJ, $\Delta S^\circ = 216$ J/K; b. $T > 958$ K 15. a. lithium oxide; b. potassium superoxide; c. sodium peroxide 17. a. $\text{Li}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{LiOH}(\text{aq})$; b. $\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$; c. $\text{LiH}(\text{s}) + \text{H}_2\text{O}(\text{l})$

$\rightarrow \text{H}_2(\text{g}) + \text{LiOH}(\text{aq})$; d. $2\text{KO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{KOH}(\text{aq}) + \text{O}_2(\text{g}) + \text{H}_2\text{O}_2(\text{aq})$ 19. $2\text{Li}(\text{s}) + 2\text{C}_2\text{H}_2(\text{g}) \rightarrow 2\text{LiC}_2\text{H}(\text{s}) + \text{H}_2(\text{g})$; oxidation-reduction 21. a. magnesium carbonate; b. barium sulfate; c. strontium hydroxide 23. $\text{CaCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$ 25. In the gas phase, linear molecules would exist:

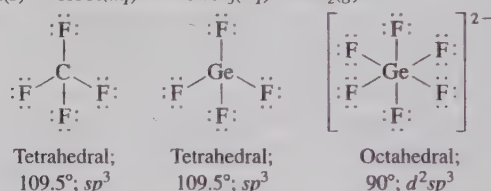


In the solid state, BeF_2 has the following extended structure:



27. $2 \times 10^{-2} M$ 29. 3.84×10^6 g Ba 31. a. AlN ; b. GaF_3 ; c. Ga_2S_3 33. $\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{B}(\text{OH})_3(\text{s})$ 35. $\text{In}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{In}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{In}_2\text{O}_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow$ no reaction; $\text{Ga}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{Ga}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{Ga}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Ga}(\text{OH})_4^-(\text{aq})$ 37. $2\text{Ga}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow 2\text{GaF}_3(\text{s})$; $4\text{Ga}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Ga}_2\text{O}_3(\text{s})$; $16\text{Ga}(\text{s}) + 3\text{S}_8(\text{s}) \rightarrow 8\text{Ga}_2\text{S}_3(\text{s})$; $2\text{Ga}(\text{s}) + \text{N}_2(\text{g}) \rightarrow 2\text{GaN}(\text{s})$; $2\text{Ga}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{GaCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$

39.



To form CF_6^{2-} , carbon would have to expand its octet of electrons. Carbon compounds do not expand their octet because of the small atomic size of carbon and because there are no low energy d orbitals on carbon to accommodate the extra electrons. 41. a. $\text{SiO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{CO}(\text{g})$; b. $\text{SiCl}_4(\text{l}) + 2\text{Mg}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{MgCl}_2(\text{s})$; c. $\text{Na}_2\text{SiF}_6(\text{s}) + 4\text{Na}(\text{s}) \rightarrow \text{Si}(\text{s}) + 6\text{NaF}(\text{s})$ 43. Lead is very toxic. As the temperature of the water increases, the solubility of Pb will increase. Drinking hot tap water from pipes containing lead solder could result in higher Pb concentrations in the body. 45. $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g})$ 47. The π electrons are free to move in graphite, thus giving it a greater conductivity (lower resistance). The electrons have the greatest mobility within the sheets of carbon atoms. Electrons in diamond are not mobile (high resistance). The structure of diamond is uniform in all directions; thus there is no directional dependence of the resistivity. 49. -390 kJ; 30.0°C 51. Strontium and calcium are both alkaline earth metals, so both have similar chemical properties. Since milk is a good source of calcium, strontium could replace some calcium in milk without much difficulty. 53. The inert-pair effect refers to the difficulty of removing the pair of valence s electrons from some of the elements in the fifth and sixth periods of the periodic table. As a result, multiple oxidation states are exhibited for the heavier elements of Groups 3A (and 4A). In^+ , In^{3+} , Tl^+ , and Tl^{3+} oxidation states are all important to the chemistry of In and Tl. 55. 3.08 57. If the compound contained $\text{Ga}(\text{II})$ it would be paramagnetic and if the compound contained $\text{Ga}(\text{I})$ and $\text{Ga}(\text{III})$, it would be diamagnetic. Paramagnetic compounds have an apparent greater mass in a magnetic field. 59. 59 atm in the gas phase; 2.8 mol CO_2/L in the wine 61. $\text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{H}_3\text{AsO}_4(\text{aq}) \rightarrow \text{PbHAsO}_4(\text{s}) + 2\text{HNO}_3(\text{aq})$ 63. $2.0 \times 10^{-37} M$ 65. Carbon is much smaller than Si and cannot form a fifth bond in the transition state.

Chapter 20

1. a. This reaction is exothermic so an increase in temperature will decrease the value of K (see Table 13.3). This lowers the amount of $\text{NH}_3(\text{g})$ produced at equilibrium. The temperature increase, therefore, must be for

kinetic reasons. As temperature increases, the reaction reaches equilibrium much faster. At low temperatures, this reaction is too slow to be of any use.

b. As $\text{NH}_3(\text{g})$ is removed, the reaction shifts right to produce more $\text{NH}_3(\text{g})$.

c. A catalyst has no effect on the equilibrium position. The purpose of a catalyst is to speed up a reaction so it reaches equilibrium more quickly.

d. When the pressure of reactants and products is high, the reaction shifts to the side that has fewer gas molecules. Since the product side contains 2 molecules of gas as compared to 4 molecules of gas on the reactant side, then the reaction shifts to the right to the products at high pressures of reactants and products.

3. Pollutants provide nitrogen and phosphorus nutrients, causing the algae to grow, which consumes oxygen, causing fish to die.

5. Plastic sulfur has long S_n chains that break down into S_8 rings.

7. Fluorine is the most electronegative element; the F_2 bond is very weak.

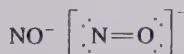
9. Helium, which does not combine with other elements, has a low mass and easily escaped the earth's gravitational pull as the planet was formed.

11. Nitrogen's small size does not provide room for all four oxygen atoms, making NO_4^{3-} unstable. Phosphorus is larger so PO_4^{3-} is more stable. To form NO_3^- , a pi bond must form. Phosphorus doesn't form strong pi bonds as readily as nitrogen.

13. a. $\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\text{Heat}} \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$;
b. $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$; **c.** $2\text{K}_3\text{P}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{PH}_3(\text{g}) + 6\text{KOH}(\text{aq})$; **d.** $\text{PBr}_3(\text{l}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{PO}_3(\text{aq}) + 3\text{HBr}(\text{aq})$;
e. $2\text{NH}_3(\text{aq}) + \text{NaOCl}(\text{aq}) \rightarrow \text{N}_2\text{H}_4(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
15. $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 10\text{H}_2\text{SO}_4(\text{aq}) + 20\text{H}_2\text{O}(\text{l}) \rightarrow 6\text{H}_3\text{PO}_4(\text{aq}) + 2\text{HF}(\text{aq}) + 10\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ **17.** 2.08 mol **19.** $\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$; $\Delta H = -590. \text{ kJ}$ **21.** $\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g})$ $\Delta G^\circ = \Delta G^\circ_{\text{f}(\text{NO})}$; NO (and some other oxides of nitrogen) have weaker bonds as compared with the triple bond of N_2 and the double bond of O_2 . Because of this, NO (and some other oxides of nitrogen) has a higher (positive) standard free energy of formation as compared to the relatively stable N_2 and O_2 molecules.

		Bond order	# unpaired e^-
M.O.	NO	2.5	1
	NO^+	3	0
	NO^-	2	2

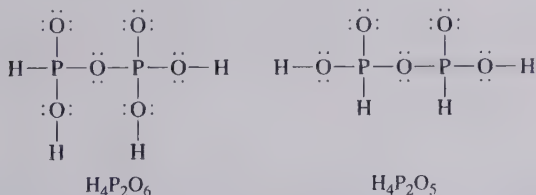
Lewis



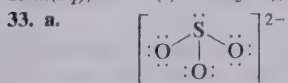
Lewis structures are not adequate for NO and NO^- . The M.O. model gives correct results for all three species. For NO, Lewis structures fail for odd-electron species. For NO^- , Lewis structures fail to predict that NO^- is paramagnetic.

25. a. $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_3$; **b.** $\text{H}_3\text{PO}_4 > \text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-}$

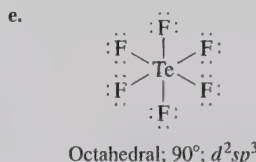
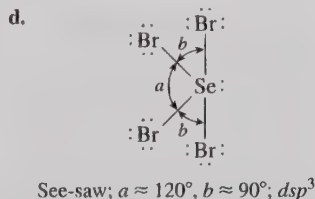
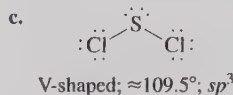
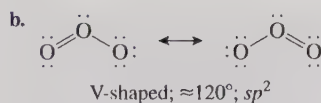
27. The acidic protons are attached to oxygen.



29. 821 nm **31. a.** $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; **b.** $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$; **c.** $2\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{Na}_2\text{S}_4\text{O}_6(\text{aq}) + 2\text{NaI}(\text{aq})$; **d.** $\text{Cu}(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CuSO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{aq})$



Trigonal pyramidal; $\approx 109.5^\circ$; sp^3



35. From the following Lewis structure, each oxygen atom has a tetrahedral arrangement of electron pairs. Therefore, bond angles $\approx 109.5^\circ$, and each O is sp^3 hybridized.

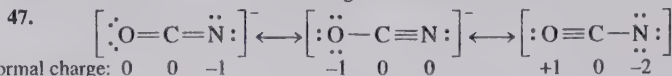


Formal charge: 0 0 0 0

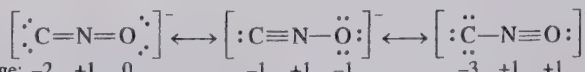
Oxidation state: -1 +1 +1 -1

Oxidation states are more useful. We are forced to assign +1 as the oxidation state for oxygen. Oxygen is very electronegative, and +1 is not a stable oxidation state for this element.

37. a. $\text{BaCl}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{HCl}(\text{g})$; **b.** $\text{BrF}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HF}(\text{aq}) + \text{HOBr}(\text{aq})$; **c.** $\text{SiO}_2(\text{s}) + 4\text{HF}(\text{aq}) \rightarrow \text{SiF}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ **39.** ClO^- can oxidize NH_3 to the somewhat toxic N_2H_4 . **41. a.** IO_4^- ; **b.** IO_3^- ; **c.** IF_2^- ; **d.** IF_4^- ; **e.** IF_6^- **43.** XeF_2 can react with oxygen to produce explosive xenon oxides and oxyfluorides. **45.** As the halogen atoms get larger, it becomes more difficult to fit three halogens around the small N.



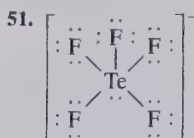
Formal charge: 0 0 -1 -1 0 0 +1 0 -2



Formal charge: -2 +1 0 -1 +1 -1 -3 +1 +1

All the resonance structures for fulminate involve greater formal charges than in cyanate, making fulminate more reactive (less stable).

49. 32 kg bacterial tissue

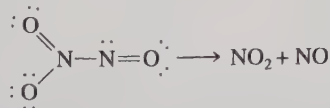


The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs, pushing the four square planar F's away from the lone pair.

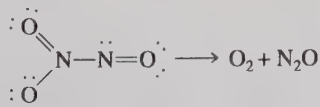
53. Release of Sr is probably more harmful. Xe is chemically unreactive. Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca. This puts the radioactive Sr in the bones; red blood cells are produced in bone marrow. Xe would not be readily incorporated in the body. The chemical properties determine

where a radioactive material may be concentrated in the body or how easily it may be excreted. The length of time of exposure and the route of exposure to radiation significantly affect the health hazard.

55. For the reaction



the activation energy must in some way involve the breaking of a nitrogen–nitrogen single bond. For the reaction



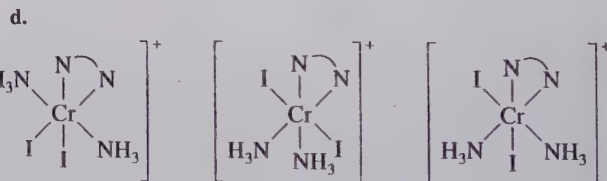
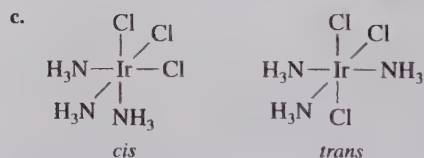
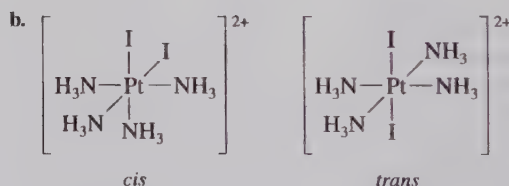
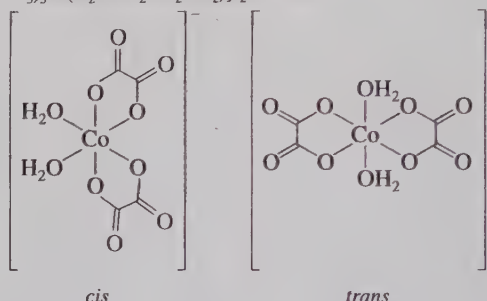
at some point nitrogen–oxygen bonds must be broken. N–N single bonds (160 kJ/mol) are weaker than N–O single bonds (201 kJ/mol). In addition, resonance structures indicate that there is more double-bond character in the N–O bonds than in the N–N bond. Thus NO_2 and NO are preferred by kinetics because of the lower activation energy. 57. a. NO ; b. NO_2 ; c. $k_{\text{cat}}/k_{\text{un}} = 2.3$; d. $\text{ClO}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{Cl}(\text{g})$; $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$; e. The Cl-catalyzed reaction is roughly 52 times faster (more efficient) than the NO-catalyzed reaction.

Chapter 21

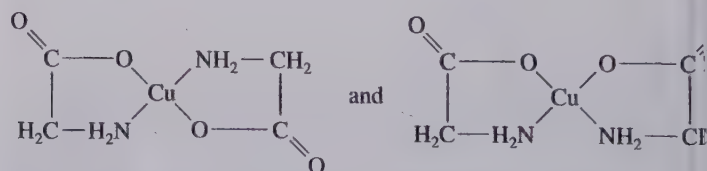
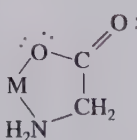
5. a. ligand: species that donates a pair of electrons to form a covalent bond to a metal ion (a Lewis base); b. chelate: ligand that can form more than one bond; c. bidentate: ligand that forms two bonds; d. complex ion: metal ion plus ligands 7. a. isomers: species with the same formulas but different properties (see text for examples of the following types of isomers); b. structural isomers: isomers that have one or more bonds that are different; c. stereoisomers: isomers that contain the same bonds but differ in how the atoms are arranged in space; d. coordination isomers: structural isomers that differ in the atoms that make up the complex ion; e. linkage isomers: structural isomers that differ in how one or more ligands are attached to the transition metal; f. geometrical isomers: (*cis-trans* isomerism) stereoisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other; g. optical isomers: stereoisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different. 9. Cu^{2+} is d^9 ; Cu^+ is d^{10} . Color results from electron transfer between split d orbitals. This cannot occur for the filled d orbitals in Cu^+ . Cd^{2+} , like Cu^+ , is also d^{10} . We would not expect $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ to be colored due to the filled d orbitals of Cd^{2+} . 11. The d -orbital splitting in tetrahedral complexes is less than one-half the d -orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case; hence all tetrahedral complexes are weak field or high spin. 13. A soluble complex ion forms: $\text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}_2\text{C}_2\text{O}_4(\text{aq}) \rightarrow 2\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 6\text{H}^+(\text{aq})$ 15. There is a steady decrease in the atomic radii of the lanthanide elements, going from left to right. As a result, the properties of the $4d$ and $5d$ elements in each group are very similar because of the similar sizes of atoms and ions. 17. Advantages: low energy cost, less air pollution; disadvantage: chemicals used are expensive 19. a. Ni: $[\text{Ar}]4s^23d^8$; b. Cd: $[\text{Kr}]5s^24d^{10}$; c. Zr: $[\text{Kr}]5s^24d^2$; d. Os: $[\text{Xe}]6s^24f^{14}5d^6$ 21. a. Ti: $[\text{Ar}]4s^23d^2$; Ti^{2+} : $[\text{Ar}]3d^2$; Ti^{4+} : $[\text{Ne}]3s^23p^6$ or $[\text{Ar}]$; b. Re: $[\text{Xe}]6s^24f^{14}5d^5$; Re^{2+} : $[\text{Xe}]4f^{14}5d^5$; Re^{3+} : $[\text{Xe}]4f^{14}5d^4$; c. Ir: $[\text{Xe}]6s^24f^{14}5d^7$; Ir^{2+} : $[\text{Xe}]4f^{14}5d^7$; Ir^{3+} : $[\text{Xe}]4f^{14}5d^6$ 23. If rain is imminent, the large amount of water vapor in the air would cause the reaction to shift to the right. The indicator would take on the color of the pink $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. 25. Test tube 1: added Cl^- reacts with Ag^+ to form the silver chloride precipitate. The net ionic equation is $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$. Test tube 2: added NH_3 reacts with Ag^+ ions to form the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$. As this complex ion forms, Ag^+ is removed from

the solution, which causes the $\text{AgCl}(\text{s})$ to dissolve. When enough NH_3 is added, then all of the silver chloride precipitate will dissolve. The equation is $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$. Test tube 3: added H^+ reacts with the weak base NH_3 to form NH_4^+ . As NH_3 is removed, Ag^+ ions are released to solution, which can then react with Cl^- to reform $\text{AgCl}(\text{s})$. The equations are $\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ag}^+(\text{aq}) + 2\text{NH}_4^+(\text{aq})$ and $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$. 27. $[\text{Co}(\text{NH}_3)_6]\text{I}_3$: 3 mol AgI ; $[\text{Pt}(\text{NH}_3)_4]\text{I}_2$: 2 mol AgI ; $\text{Na}_2[\text{PtCl}_6]$: 0 mol AgI ; $[\text{Cr}(\text{NH}_3)_4]\text{I}_2$: 1 mol AgI . 29. a. pentaamminechlororuthenium(III) ion; b. hexacyanoferrate(II) ion; c. tris(ethylenediamine)manganese(II) ion; d. pentaamminenitrocobalt(III) ion 31. a. hexaamminecobalt(II) chloride; b. hexaaquacobalt(III) iodide; c. potassium tetrachloroplatinate(II); d. potassium hexachloroplatinate(II); e. pentaamminechlorocobalt(III) chloride; f. triaminetritrocobalt(III) 33. a. $\text{K}_2[\text{CoCl}_4]$; b. $[\text{Pt}(\text{H}_2\text{O})(\text{CO})_3]\text{Br}_2$; c. $\text{Na}_3[\text{Fe}(\text{CN})_2(\text{C}_2\text{O}_4)_2]$; d. $[\text{Cr}(\text{NH}_3)_3\text{Cl}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)]\text{I}_2$

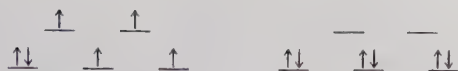
35. a.



37.



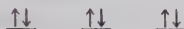
39. SCN^- , NO_2^- , and OCN^- can form linkage isomers; all are able to bond to the metal ion in two different ways. 41. $\text{Cr}(\text{acac})_3$ and *cis*- $\text{Cr}(\text{acac})_2(\text{H}_2\text{O})_2$ are optically active.

43. a. Fe^{2+} b. Fe^{3+} c. Ni^{2+} 

High spin

Low spin

45. weak field 47. a. 0; b. 2; c. 2 49. The violet complex ion absorbs yellow-green light ($\lambda \approx 570 \text{ nm}$), the yellow complex ion absorbs blue light ($\lambda \approx 450 \text{ nm}$), and the green complex ion absorbs red light ($\lambda \approx 650 \text{ nm}$). The violet complex ion is $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, the yellow complex ion is $\text{Cr}(\text{NH}_3)_6^{3+}$, and the green complex ion is $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$. 51. CoBr_4^{2-} is a tetrahedral complex ion, while CoBr_6^{4-} is an octahedral complex ion. Since tetrahedral d -orbital splitting is less than one-half the octahedral d -orbital splitting, the octahedral complex ion (CoBr_6^{4-}) will absorb higher-energy light, which will have a shorter wavelength than $3.4 \times 10^{-6} \text{ m}$ ($E = hc/\lambda$). 53. 5 55. a. -11 kJ ; b. $\Delta H^\circ = 172.5 \text{ kJ}$; $\Delta S^\circ = 176 \text{ J/K}$; $T > 980. \text{ K}$ 57. $[\text{Cr}(\text{NH}_3)_5\text{I}]_2$; octahedral 59. a. 2; b. 3; c. 4; d. 4 61. a. optical isomerism



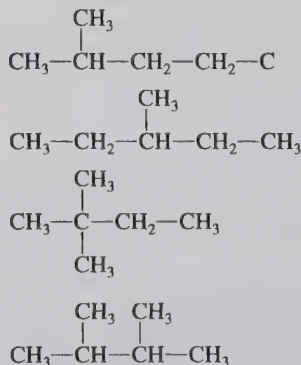
63. Octahedral Cr^{2+} complexes should be used. Cr^{2+} : $[\text{Ar}]3d^4$; High-spin (weak-field) Cr^{2+} complexes have four unpaired electrons and low-spin (strong-field) Cr^{2+} complexes have two unpaired electrons. Ni^{2+} : $[\text{Ar}]3d^8$; Octahedral Ni^{2+} complexes will always have two unpaired electrons, whether high or low spin. Therefore, Ni^{2+} complexes cannot be used to distinguish weak- from strong-field ligands by examining magnetic properties. Alternatively, the ligand field strengths can be measured using visible spectra. Either Cr^{2+} or Ni^{2+} complexes can be used for this method. 65. $\text{Pb}(\text{OH})_2$ will not form since Q is less than K_{sp} . 67. 60 69. a. -0.26 V ; b. From standard reduction potentials, Co^{3+} ($\mathcal{E}^\circ = 1.82 \text{ V}$) is a much stronger oxidizing agent than $\text{Co}(\text{en})_3^{3+}$ ($\mathcal{E}^\circ = -0.26 \text{ V}$); c. In aqueous solution, Co^{3+} forms the hydrated transition metal complex, $\text{Co}(\text{H}_2\text{O})_6^{3+}$. In both complexes, $\text{Co}(\text{H}_2\text{O})_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$, cobalt exists as Co^{3+} , which has 6 d electrons. If we assume a strong-field case for each complex ion, then the d -orbital splitting diagram for each has the six electrons paired in the lower-energy t_{2g} orbitals. When each complex ion gains an electron, the electron enters the higher-energy e_g orbitals. Since en is a stronger-field ligand than H_2O , then the d -orbital splitting is larger for $\text{Co}(\text{en})_3^{3+}$, and it takes more energy to add an electron to $\text{Co}(\text{en})_3^{3+}$ than to $\text{Co}(\text{H}_2\text{O})_6^{3+}$. Therefore, it is more favorable for $\text{Co}(\text{H}_2\text{O})_6^{3+}$ to gain an electron than for $\text{Co}(\text{en})_3^{3+}$ to gain an electron. 71. No, since in all three cases six bonds are formed between Ni^{2+} and nitrogen. So ΔH values should be similar. ΔS° for formation of the complex ion is most negative for 6 NH_3 molecules reacting with a metal ion (7 independent species become 1). For penten reacting with a metal ion, 2 independent species become 1, so ΔS° is the least negative. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the more favorable ΔS° is for the formation of the complex ion, and the larger the formation constant.

73. d_z^2
 $d_{x^2-y^2}, d_{xy}$
 d_{xz}, d_{yz}

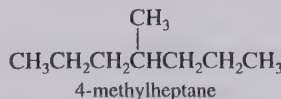
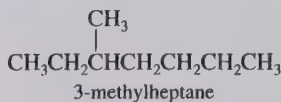
Chapter 22

1. A consecutive chain of C atoms. They are not all in a true straight line since the bond angles at each carbon are 109.5° . 3. Resonance: All atoms are in the same position. Only the position of π electrons are different. Isomerism: Atoms are in different locations in space. Isomers are distinctly different substances. Resonance is the use of more than one Lewis structure to describe the bonding in a single compound. Resonance structures are not isomers. 5. Substitution: an atom or group is replaced by another atom or group; e.g., H in benzene is replaced by Cl: $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{Catalyst}}$

$\text{C}_6\text{H}_5\text{Cl} + \text{HCl}$; addition: atoms or groups are added to a molecule; e.g., Cl_2 adds to ethene: $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ 7. A thermoplastic polymer can be remelted; a thermoset polymer cannot be softened once it is formed. 9. Crosslinking makes a polymer more rigid. 11. In nylon, hydrogen bonding interactions occur due to the presence of $[\text{N}-\text{H}]$ bonds in the polymer. For a given polymer chain length, there are more $[\text{N}-\text{H}]$ groups in nylon-46 as compared to nylon-6. Hence, nylon-46 forms a stronger polymer as compared to nylon-6 due to the increased hydrogen bonding interactions. 13. Primary: the amino acid sequence in the protein. The covalent bonds (peptide linkages) between amino acids maintain the primary structure. Secondary: includes structural features known as α -helix or pleated sheet. Both are maintained mostly through hydrogen bonding interactions. Tertiary: the overall shape of a protein, long and narrow or globular. Maintained by hydrophobic and hydrophilic interactions, such as salt linkages, hydrogen bonds, disulfide linkages, and dispersion forces. 15. All amino acids can act as both a weak acid and a weak base; this ability is the requirement for a buffer. The weak acid is the carboxylic end of the amino acid, and the weak base is the amine end of the amino acid. 17. Hydrogen bonding interactions occur between water and the many $[-\text{OH}]$ groups on starch. 19. nitrogen atoms with lone pairs of electrons 21. A deletion may change the entire code for a protein. A substitution will change only one single amino acid in a protein.

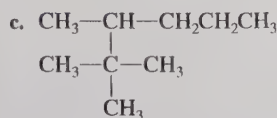
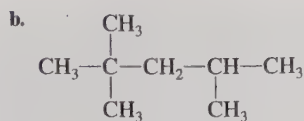
23. $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ 

25. a. CH_3
 $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 2-methylheptane



b. CH_3 CH_3
 $\text{CH}_3-\text{C}-\text{C}-\text{CH}_3$
 CH_3 CH_3
 2,2,3,3-tetramethylbutane

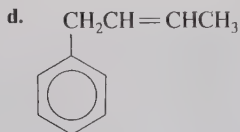
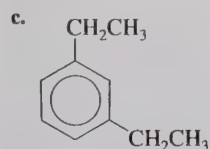
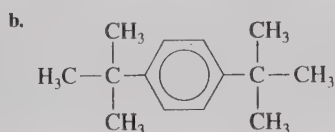
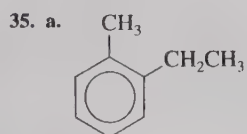
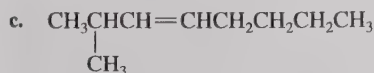
27. a. $\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2\text{CH}_3$
 CH_3



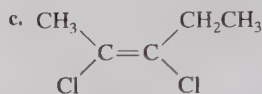
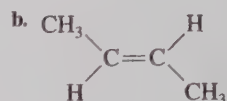
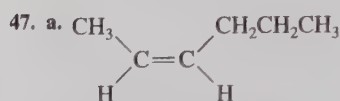
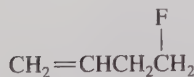
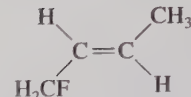
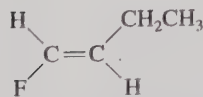
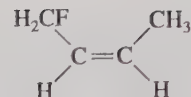
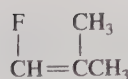
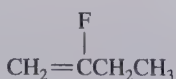
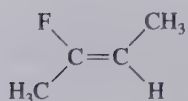
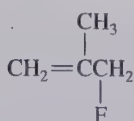
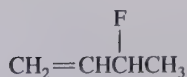
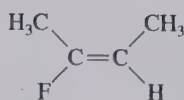
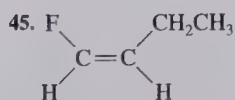
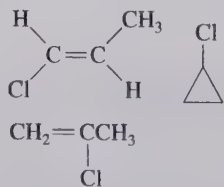
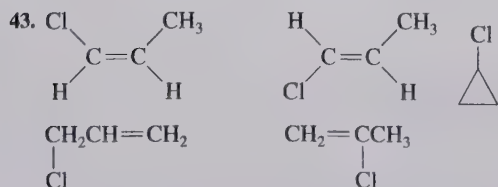
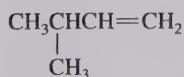
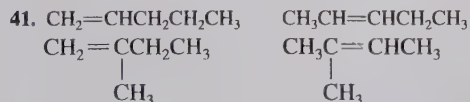
d. 2,2,3-trimethylhexane

29. a. 2,2,4-trimethylhexane; b. 5-methylnonane; c. 2,2,4,4-tetramethylpentane; d. 3-ethyl-3-methyloctane 31. a. 1-butene; b. 4-methyl-2-hexene; c. 2,5-dimethyl-3-heptene

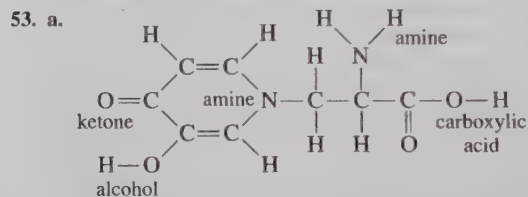
33. a. $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$; b. $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_2\text{CH}_3$;



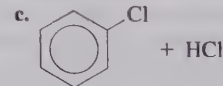
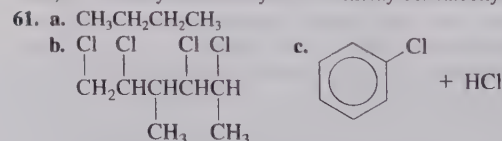
37. a. 1,3-dichlorobutane; b. 1,1,1-trichlorobutane; c. 2,3-dichloro-2,4-dimethylhexane; d. 1,2-difluoroethane 39. [31], compounds b and c; [33], all compounds



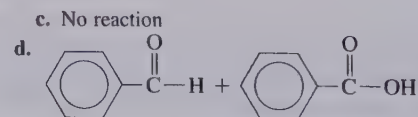
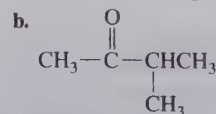
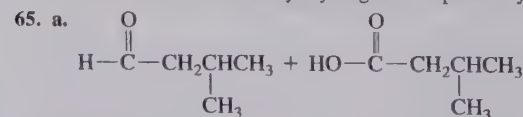
49. a. 3 monochloro isomers of *n*-pentane; b. 4 monochloro isomers of 2-methylbutane; c. 3 monochloro isomers of 2,4-dimethylpentane; d. 4 monochloro isomers of methylcyclobutane 51. a. ketone; b. aldehyde; c. carboxylic acid; d. amine

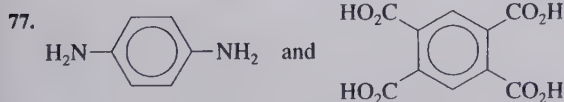
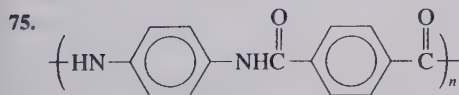
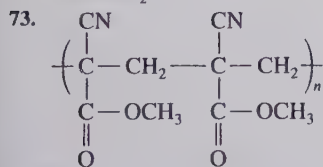
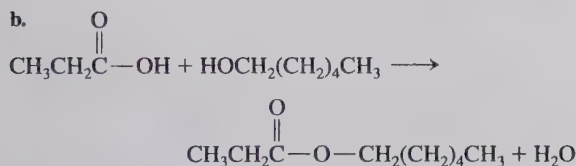
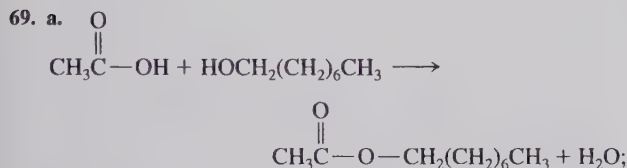
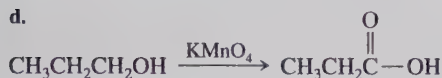
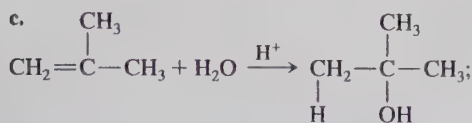
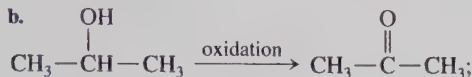
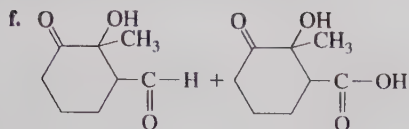
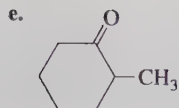


b. 5 carbons in ring and the carbon in $-\text{CO}_2\text{H}$: sp^2 ; the other two carbons: sp^3 ; c. 24 sigma bonds, 4 pi bonds 55. a. 3-chloro-1-butanol, primary; b. 3-methyl-3-hexanol, tertiary; c. 2-methylcyclopentanol, secondary 57. 1-pentanol; 2-pentanol; 3-pentanol; 2-methyl-1-butanol; 2-methyl-2-butanol; 3-methyl-2-butanol; 3-methyl-1-butanol; 2,2-dimethyl-1-propanol; 6 ethers 59. a. 4,5-dichloro-3-hexanone; b. 2,3-dimethylpentanal; c. 3-methylbenzaldehyde or *m*-methylbenzaldehyde

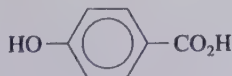


63. For the iron-catalyzed reaction, one of the *ortho* or *para* hydrogens in benzene is replaced by chlorine. When an iron catalyst is not present, then the benzene hydrogens are unreactive, which is seen for the light-catalyzed reaction where one of the methyl hydrogens is replaced by chlorine.



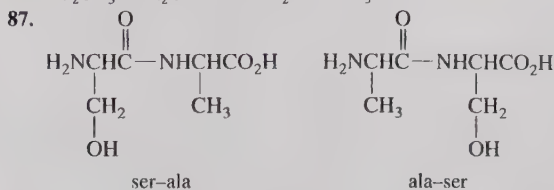


79. Divinylbenzene inserts itself into two adjacent polymer chains and bonds them together. The chains cannot move past each other because of the crosslinks making the polymer more rigid. 81. a. The polymer from 1,2-diaminoethane and terephthalic acid is stronger because of the possibility of hydrogen bonding between chains. b. The polymer of

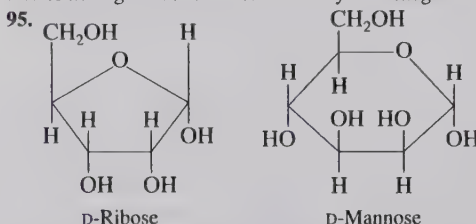


is more rigid because the chains are stiffer due to the rigid benzene rings in the chains. c. Polyacetylene is $n\text{HC}\equiv\text{CH} \rightarrow \text{-(CH}=\text{CH)}_n$. Polyacety-

lene is more rigid because the double bonds in the chains make the chains stiffer. 83. a. serine; tyrosine; threonine; b. aspartic acid; glutamic acid; c. histidine; lysine; arginine; tryptophan; d. glutamine; asparagine 85. a. aspartic acid and phenylalanine; b. Aspartame contains the methyl ester of phenylalanine. This ester can hydrolyze to form methanol, $\text{R-CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{RCO}_2\text{H} + \text{CH}_3\text{OH}$.

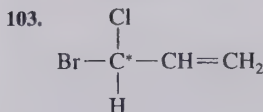
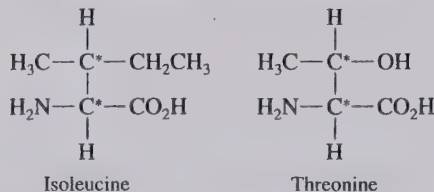


89. a. Six tetrapeptides are possible. From NH_2 to CO_2H end: phe-phe-gly-gly, gly-gly-phe-phe, gly-phe-phe-gly, phe-gly-gly-phe, phe-gly-phe-gly, gly-phe-gly-phe b. Twelve tetrapeptides are possible. From NH_2 to CO_2H end: phe-phe-gly-ala, phe-phe-ala-gly, phe-gly-phe-ala, phe-gly-ala-phe, phe-ala-phe-gly, phe-ala-gly-phe, gly-phe-phe-ala, gly-phe-ala-phe, gly-ala-phe-phe, ala-phe-phe-gly, ala-phe-gly-phe, ala-gly-phe-phe 91. Ionic: his, lys, or arg with asp or glu; hydrogen bonding: ser, glu, tyr, his, arg, asn, thr, asp, gln, or lys with any amino acid; covalent: cys with cys; London dispersion: all amino acids with nonpolar R groups (gly, ala, pro, phe, ile, trp, met, leu, val); dipole-dipole: tyr, thr, and ser with each other 93. Glutamic acid has a polar R group and valine has a nonpolar R group. The change in polarity of the R groups could affect the tertiary structure of hemoglobin and affect the ability of hemoglobin to bond to oxygen.



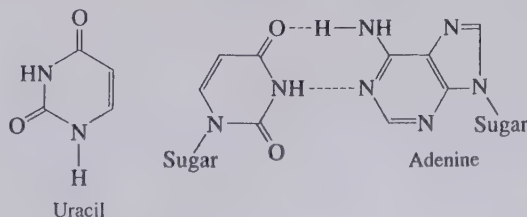
97. aldohexose: glucose, mannose, galactose; aldopentose: ribose, arabinose; ketohexose: fructose; ketopentose: ribulose 99. They differ in the orientation of a hydroxy group on a particular carbon. Starch is composed from α -D-glucose, and cellulose is composed from β -D-glucose.

101. The chiral carbons are marked with asterisks.

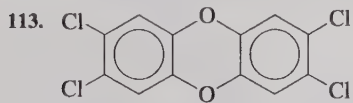


is optically active. The chiral carbon is marked with an asterisk.

105. C-C-A-G-A-T-A-T-G 107. Uracil will H-bond to adenine.



109. a. glu: CTT, CTC; val: CAA, CAG, CAT, CAC; met: TAC; trp: ACC; phe: AAA, AAG; asp: CTA, CTG; b. ACC-CTT-AAA-TAC or ACC-CTC-AAA-TAC or ACC-CTT-AAG-TAC or ACC-CTA-AAG-TAC; c. four (see answer in part b); d. met-asp-phe e. TAC-CTA-AAG; TAC-CTA-AAA; TAC-CTG-AAA **111.** $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, 1,2-dichloroethane; there is free rotation about the C—C single bond, which doesn't lead to different compounds. $\text{CHCl}=\text{CHCl}$, 1,2-dichloroethene; there is no rotation about the C=C double bond. This creates the *cis* and *trans* isomers, which are different compounds.

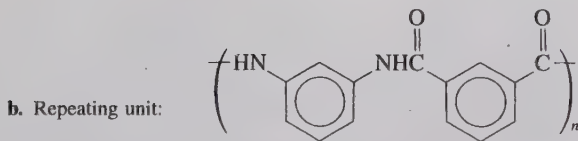
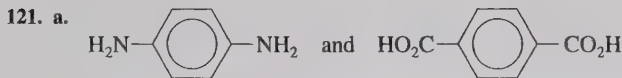


There are many possibilities for isomers. Any structure with four chlorines replacing four hydrogens in any of the numbered positions would be an isomer; i.e., 1,2,3,4-tetrachloro-dibenzo-*p*-dioxin is a possible isomer.

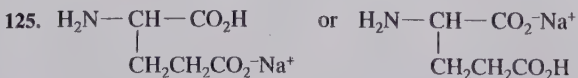
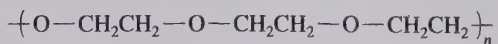
115. Alcohols consist of two parts, the polar OH group and the nonpolar hydrocarbon chain attached to the OH group. As the length of the nonpolar hydrocarbon chain increases, the solubility of the alcohol decreases. In methyl alcohol (methanol), the polar OH group can override the effect of the nonpolar CH₃ group, and methyl alcohol is soluble in water. In stearyl alcohol, the molecule consists mostly of the long nonpolar hydrocarbon chain, so it is insoluble in water.

117. *n*-hexane, 69°C; pentanol, 103°C; 1-pentanol, 137°C; butanoic acid, 164°C.

119. 1-butene

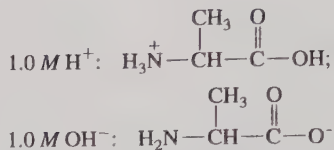


The two polymers differ in the substitution pattern on the benzene rings. The Kevlar chain is straighter, and there is more efficient hydrogen bonding between Kevlar chains than between Nomex chains. **123. a.** The bond angles in the ring are about 60° . VSEPR predicts bond angles close to 109° . The bonding electrons are much closer together than they prefer, resulting in strong electron-electron repulsions. Thus ethylene oxide is unstable (reactive). **b.** The ring opens up during polymerization and the monomers link together through the formation of O—C bonds.

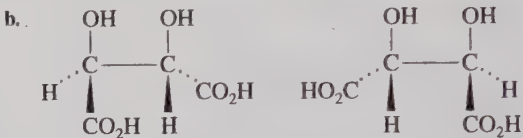


The first structure is MSG, which is impossible for you to predict. 127. In the reaction, P—O and O—H bonds are broken and P=O and O—H bonds are formed. Thus $\Delta H \approx 0$. $\Delta S < 0$, since two molecules are going to form one molecule. Thus $\Delta G > 0$, not spontaneous.

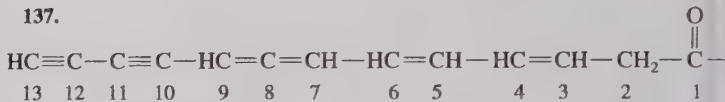
129.



131. The Cl^- ions are lost upon binding to DNA. The dimension is just right for cisplatin to bond to two adjacent bases in one strand of the helix, which inhibits DNA synthesis. **133.** 6.07 **135. a.** No; the mirror image is superimposable.

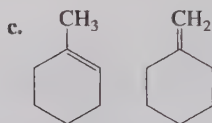


137.



139. a. $\text{CH}_3\text{CHCH}_2\text{CH}_3$
|
 CH_3

b. $\text{CH}_2=\text{CCH}_3$
 $\quad\quad\quad |$
 $\quad\quad\quad \text{CH}_3$

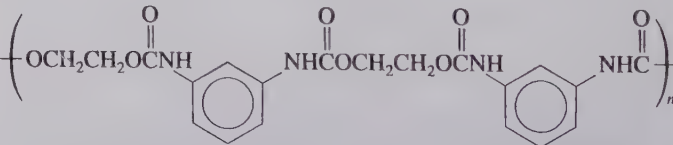


d. $\text{CH}_2=\text{CHCH}_3$

e. $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$ $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CHCH}_2\text{CH}_2 \\ | \\ \text{OH} \end{array}$ $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2-\text{C}-\text{CH}_3 \\ | \quad | \\ \text{OH} \quad \text{CH}_3 \end{array}$

141.



143. a. The temperature of the rubber band increases when it is stretched; **b.** exothermic (heat is released); **c.** As the chains are stretched, they line up more closely resulting in stronger dispersion forces between the chains. Heat is released as the strength of the intermolecular forces increases. **d.** ΔG is positive and ΔS is negative; **e.** The structure of the stretched polymer chains is more ordered than in unstretched rubber. Disorder decreases as the rubber band is stretched.

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Noble gases
↑
18 Halogens

58	Ce	140.1	59	Pr	140.9	60	Nd	144.2	61	Pm	(145)	62	Sm	150.4	63	Eu	152.0	64	Gd	157.3	65	Tb	158.9	66	Dy	162.5	67	Ho	164.9	68	Er	167.3	69	Tm	168.9	70	Yb	173.0	71	Lu	175.0
90	Th	232.0	91	Pa	(231)	92	U	238.0	93	Np	(237)	94	Pu	(244)	95	Am	(243)	96	Cm	(247)	97	Bk	(247)	98	Cf	(251)	99	Es	(252)	100	Fm	(257)	101	Md	(258)	102	No	(259)	103	Lr	(260)

† Actinides

bottom # is 100/6 in g/mol

Group numbers 1-18 represent the system recommended by the International Union of Pure and Applied Chemistry.

Table of Atomic Masses*

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227] [§]	Hafnium	Hf	72	178.5	Promethium	Pm	61	[145]
Aluminum	Al	13	26.98	Hassium	Hs	108	[265]	Protactinium	Pa	91	[231]
Americium	Am	95	[243]	Helium	He	2	4.003	Radium	Ra	88	226
Antimony	Sb	51	121.8	Holmium	Ho	67	164.9	Radon	Rn	86	[222]
Argon	Ar	18	39.95	Hydrogen	H	1	1.008	Rhenium	Re	75	186.2
Arsenic	As	33	74.92	Indium	In	49	114.8	Rhodium	Rh	45	102.9
Astatine	At	85	[210]	Iodine	I	53	126.9	Rubidium	Rb	37	85.47
Barium	Ba	56	137.3	Iridium	Ir	77	192.2	Ruthenium	Ru	44	101.1
Berkelium	Bk	97	[247]	Iron	Fe	26	55.85	Rutherfordium	Rf	104	[261]
Beryllium	Be	4	9.012	Krypton	Kr	36	83.80	Samarium	Sm	62	150.4
Bismuth	Bi	83	209.0	Lanthanum	La	57	138.9	Scandium	Sc	21	44.96
Bohrium	Bh	107	[264]	Lawrencium	Lr	103	[260]	Selenium	Se	34	[263]
Boron	B	5	10.81	Lead	Pb	82	207.2	Selenium	Se	34	78.96
Bromine	Br	35	79.90	Lithium	Li	3	6.941	Silicon	Si	14	28.09
Cadmium	Cd	48	112.4	Lutetium	Lu	71	175.0	Silver	Ag	47	107.9
Calcium	Ca	20	40.08	Magnesium	Mg	12	24.31	Sodium	Na	11	22.99
Californium	Cf	98	[251]	Manganese	Mn	25	54.94	Strontium	Sr	38	87.62
Carbon	C	6	12.01	Meitnerium	Mt	109	[268]	Sulfur	S	16	32.07
Cerium	Ce	58	140.1	Mendelevium	Md	101	[258]	Tantalum	Ta	73	180.9
Cesium	Cs	55	132.90	Mercury	Hg	80	200.6	Technetium	Tc	43	[98]
Chlorine	Cl	17	35.45	Molybdenum	Mo	42	95.94	Tellurium	Te	52	127.6
Chromium	Cr	24	52.00	Neodymium	Nd	60	144.2	Terbium	Tb	65	158.9
Cobalt	Co	27	58.93	Neon	Ne	10	20.18	Thallium	Tl	81	204.4
Copper	Cu	29	63.55	Neptunium	Np	93	[237]	Thorium	Th	90	232.0
Curium	Cm	96	[247]	Nickel	Ni	28	58.69	Thulium	Tm	69	168.9
Dubnium	Db	105	[262]	Niobium	Nb	41	92.91	Tin	Sn	50	118.7
Dysprosium	Dy	66	162.5	Nitrogen	N	7	14.01	Titanium	Ti	22	47.88
Einsteinium	Es	99	[252]	Nobelium	No	102	[259]	Tungsten	W	74	183.9
Erbium	Er	68	167.3	Osmium	Os	76	190.2	Uranium	U	92	238.0
Europium	Eu	63	152.0	Oxygen	O	8	16.00	Vanadium	V	23	50.94
Fermium	Fm	100	[257]	Palladium	Pd	46	106.4	Xenon	Xe	54	131.3
Fluorine	F	9	19.00	Phosphorus	P	15	30.97	Ytterbium	Yb	70	173.0
Francium	Fr	87	[223]	Platinum	Pt	78	195.1	Yttrium	Y	39	88.91
Gadolinium	Gd	64	157.3	Plutonium	Pu	94	[244]	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Po	84	[209]	Zirconium	Zr	40	91.22
Germanium	Ge	32	72.59	Potassium	K	19	39.10				
Gold	Au	79	197.0	Praseodymium	Pr	59	140.9				

*The values given here are to four significant figures where possible. [§]A value given in parentheses denotes the mass of the longest-lived isotope.

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Physical Constants

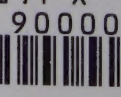
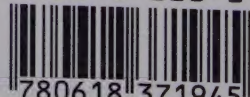
Constant	Symbol	Value
Atomic mass unit	amu	1.66054×10^{-27} kg
Avogadro's number	N	6.02214×10^{23} mol ⁻¹
Bohr radius	a_0	5.292×10^{-11} m
Boltzmann constant	k	1.38066×10^{-23} J/K
Charge of an electron	e	1.60218×10^{-19} C
Faraday constant	F	96,485 C/mol
Gas constant	R	8.31451 J/K · mol 0.08206 L · atm/K · mol
Mass of an electron	m_e	9.10939×10^{-31} kg 5.48580×10^{-4} amu
Mass of a neutron	m_n	1.67493×10^{-27} kg 1.00866 amu
Mass of a proton	m_p	1.67262×10^{-27} kg 1.00728 amu
Planck's constant	h	6.62608×10^{-34} J · s
Speed of light	c	2.99792458×10^8 m/s



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